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A STUDY ON THE DECOMPOSITION OF TRIPOSITIVE SILVER COMPLEX : SILVER ETHYLENEDIBIGUANIDE NITRATE

By Debabrata Sen and Priyadaranjan Rây

The rate of decomposition of the tripositive silver complex, silver ethylenedibiguanide nitrate, has been studied in water, as well as in nitric acid solutions at 25°, 35° and 45°. The mechanism of the decomposition has been discussed and is believed to differ in the water and in the acid solutions. The decomposition reaction has been found to follow the law of unimolecular reaction. From the temperature variation of the specific reaction rate, the activation energy of the reaction, both in pure water and in nitric acid solutions, has been determined.

The stability of the ethylenedibiguanide complex of tripositive silver in aqueous solutions has been determined from the equilibrium constant of the reaction between the complex and the hydrogen ion, and the acid dissociation constant of the base ethylenedibiguanide (Sen, Ghose and Rây, this *Journal*, 1950, **27**, 619). The value obtained for the instability constant was found to be of the order of 10^{-52}, representing a very high degree of stability of the complex. Nevertheless, it is found to decompose slowly in solution with time, on keeping.

It was therefore considered interesting to study the kinetics of the decomposition of the tripositive silver complex into univalent silver ion and ethylenedibiguanide. The reaction can be followed by the measurement of total tripositive silver remaining in solution after definite time intervals. This was carried out by titrating the iodine liberated by the substance from KI in acetic acid solution. It was found that the decomposition followed practically the equation for unimolecular reaction:

$$\frac{-d\,(a-x)}{dt} = k\,(a-x).$$

Hence $kt = \ln a/a-x,$

or $kt = 2.303 \log a/a-x\ ;$

where k = velocity constant at a particular temperature, a = initial conc. of the complex, and $a-x$ = conc. of the total tripositive silver after a time t.

By plotting the value of $\log a/a-x$ against the different time intervals t, a straight line curve is obtained showing that the reaction is unimolecular, and the slope of the curve gives the value of unimolecular velocity constant at a particular temperature.

Applying Arrhenius's equation

$$\frac{d \ln k}{dt} = \frac{E}{RT^2}$$

and integrating, we get

$$\ln k = -\frac{E}{RT} + C$$

where C = a constant and E = activation energy.

The value of E was obtained by plotting the values of $\ln k$ against $1/T$ at different temperatures. The slope of the curve gives the values of $-E/R$. Thus, the activation energy E of the given reaction can be easily calculated.

Knowing the activation energy, the value of the Arrhenius's constant A or PZ can be calculated from the following equation,

$$k = A.e^{-E/R_T}$$

The Arrhenius's constant, known as the frequency factor, is equal to the product of P, the probability or steric factor and Z, the collision number. The velocity constant of a reaction depends both on A and E. The energy of activation of a reaction does not vary greatly with temperature, while the Arrhenius's constant A does.

Fig. 1

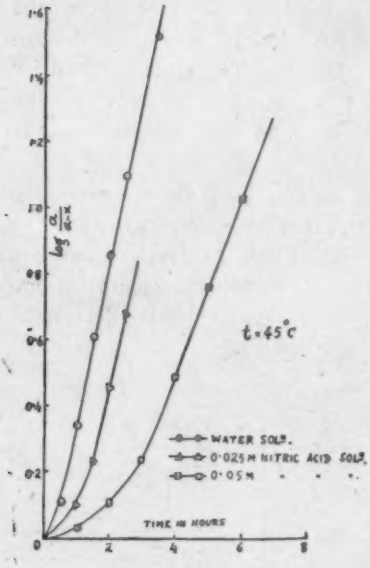
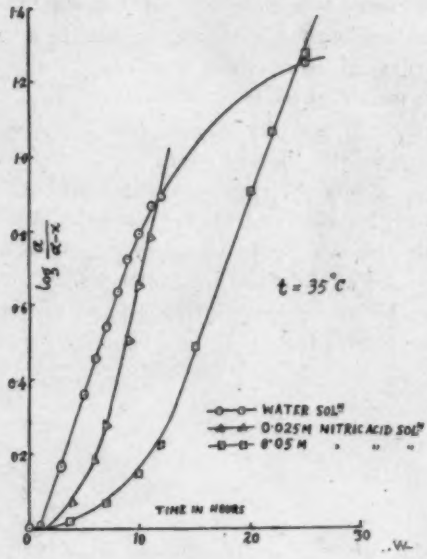


Fig. 2



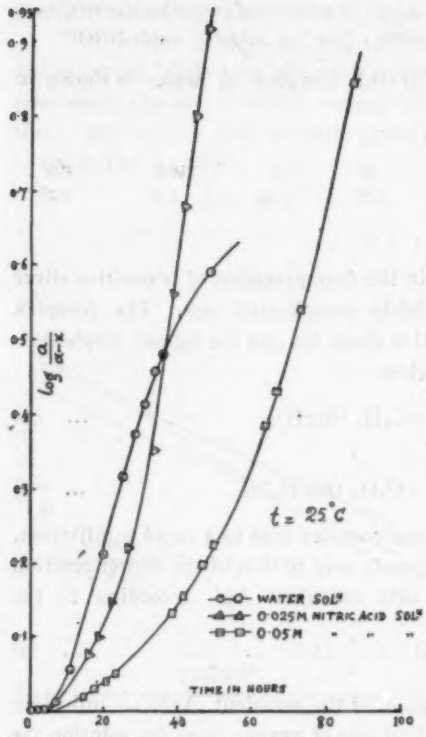
In the present paper the rate of decomposition of ethylenedibiguanide complex of tripositive silver was studied at 45°, 35° and 25°, as it was expected to throw some light regarding the mechanism of the reactions leading to the decomposition of the complex tripositive silver into simple univalent silver ion.

EXPERIMENTAL

Silver ethylenedibiguanide nitrate was prepared and purified by recrystallisation from hot 2N-HNO_3, following the procedure described by Rây and Chakravarty (this *Journal*, 1944, **21**, 41). {Found : Ag, 20.62 ; Ag^{3+}, 20.65. [Ag. C_2H_4 $(BigH)_2$] $(NO_3)_3$ requires Ag, 20.69; Ag^{3+}, 20.69 per cent}.

'Analar' sodium thiosulphate was dissolved in water to make a $M/50$ solution. To this was added a little amyl alcohol. The solution was kept for 4 to 5 days, filtered and poured into a bottle from which a microburette can be filled by pumping. The sodium thiosulphate was then standardised against potassium bi-iodate.

Fig. 3



Study of the Reaction Rate.—Silver^{III} ethylenedibiguanide nitrate was dissolved in conductivity water, 0.025M nitric acid and in 0.05M nitric acid respectively. The water and the acid solutions were all kept in the thermostat at a definite temperature at which the reaction was studied. After dissolving the complex nitrate the three flasks were immediately kept in the thermostat and an aliquot portion pipetted out and titrated iodometrically against standard sodium thiosulphate solution. The titrations were carried out at intervals of time till an appreciable titre value could be obtained. The results obtained are represented graphically in Figs. 1-7.

The values of k at different temperatures in water and in acid solutions, obtained from the straight portions of the curves, are given below in Table I.

TABLE I

Values of k.

	At 25°.	At 35°.	At 45°.
Water	1.186×10^{-5}	5.542×10^{-5}	3.20×10^{-4}
0.025M-HNO_3	2.56×10^{-5}	7.89×10^{-5}	2.87×10^{-4}
0.05M-HNO_3	...	5.28×10^{-5}	1.71×10^{-4}

The value of E, the activation energy, as obtained from Fig. 4, is given by 27, 800 cal./mol. in water solution and 18,650 cal./mol. in acid solutions respectively.

The values of log A (Arrhenius's constant) at different temperatures obtained from the equation are shown in Table II.

TABLE II

	At 25°.	At 35°.	At 45°.
log A	15.32	15.30	15.49 in water
"	8.99	9.04	9.3 " 0.025M-NHO_3
"	..	8.86	8.97 " 0.05M-HNO_3

The variation of p_H of a 0.01M solution of the complex in water is shown in Table III.

TABLE III

Time (hours) ...	0	3	22.5	48	71.5	118.5	169
p_H ...	3.08	3.21	3.71	3.77	3.99	4.28	4.28

DISCUSSION

The mechanism of the reaction involved in the decomposition of tripositive silver complex to the simple univalent silver ion is a fairly complicated one. The complex first dissociates into the constituents, a tripositive silver ion and the ligand ethylenedibiguanide or ethylenedibiguanide ion, as shown below:

$$[Ag.C_2H_4(BigH)_2]^{3+} \rightleftarrows Ag^{3+} + C_2H_4(BigH)_2 \quad \ldots (1)$$

$$[Ag.C_2H_4(BigH)_2]^{3+} + 2H^+ \rightleftarrows Ag^{3+} + C_2H_4(BigH_2^+)_2 \quad \ldots (2)$$

The reactions involved in the dissociation of the complex lead to a rapid equilibrium. So, the measurement of the reaction rate corresponds only to that of the slower reaction involved in the decomposition of tervalent Ag^{3+} into univalent Ag^+ according to the following scheme:

$$Ag^{3+} + H_2O \rightleftarrows Ag^+ + 2H^+ + \frac{1}{2}O_2 \quad \ldots \quad \ldots (3)$$

The equation (3) suggests that the decomposition of the tervalent Ag^{3+} to univalent Ag^+ is a unimolecular reaction. With the gradual loss of oxygen from the solution the reaction ultimately proceeds to completion, when the red colour of the solution of the complex is ultimately discharged. Equation (3) further points to the fact that acids should somewhat stabilise the tervalent silver ion.

At 45°, the straight line decomposition curve clearly indicates that the decomposition of the tervalent silver complex at that temperature is practically a unimolecular reaction. An examination of the decomposition curves in water and in nitric acid solutions at this temperature shows that the stability of the tervalent silver ion increases with acid concentration. This is in agreement with the properties of the complex. The complex can be boiled in nitric acid solution without appreciable decomposition. But in aqueous solution the complex decomposes on boiling.

At 35°, the curve for the water solution is not a straight line throughout the decomposition. After about 20 hours, the curve bends showing the influence of a secondary factor in the reaction. For the acid solutions, there is a gradual and slow rise of the curve to begin with, but then it goes straight up to the last. The same phenomenon is observed to a greater extent at 25°. The slow rise of the curve at the beginning is to be found for both the water and acid solutions for all temperatures, more so at lower than at higher temperatures, and more for acid than for water solutions, and becomes

increasingly prominent as the strength of the acid increases. This seems to suggest that there is a period of inhibition which is more or less eliminated with the rise of temperature, but prolonged with the increase of acid concentration. The acid or the presence of hydrogen ion seems to stabilise the tervalent silver ion in solution.

The values of k at 25° and 35° for water and acid solutions appear to be, however, not in accord with this observation, as these values are derived only from the straight portions of the curves, which correspond to different intervals for acid and water solutions, and as the first portions of the acid curves are left out of consideration because of the inhibiting effect.

Fig. 4

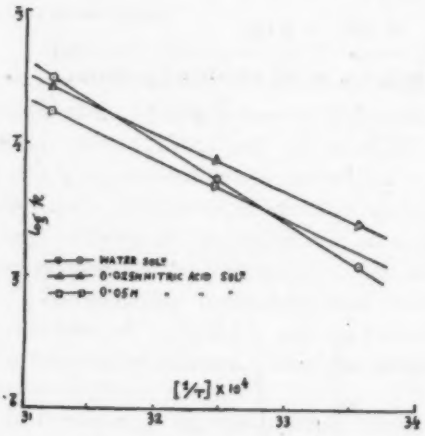
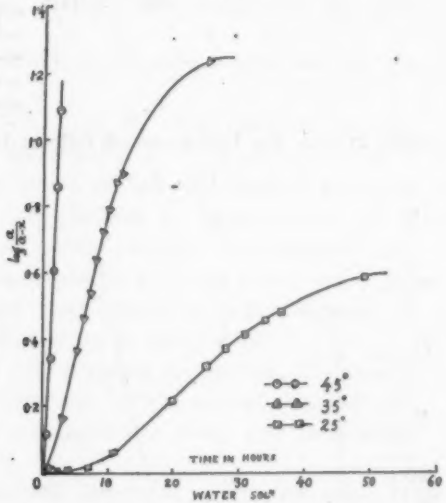


Fig. 5



The bending of the curve in the case of water solution towards the end may be explained as follows. The dissociation of the complex may take place by two ways, one being simple dissociation (Eqn. 1) and the other by reaction with hydrogen ion (Eqn.2). In acid medium, the reaction (2) mainly occurs; the rate of formation of Ag^{3+} by (1) being too small in comparison with that formed by (2). In aqueous solution, both the reactions occur to a more or less equal extent. But these two reactions lead to a very rapid equilibrium. Table III shows that the solution of the complex in pure water, to begin with, is acidic due to the hydrolysis of the complex salt itself. But as the decomposition proceeds, the p_H of the solution on complete decomposition reaches the same p_H value as that of the ethylenedibiguanide nitrate. So, with the increase of p_H, the reaction (2) is gradually retarded and the formation of tervalent silver ion results mostly from the reaction (1). At room temperature, the amount of Ag^{3+} formed by this reaction is very small and consequently the decomposition of the complex also becomes slow towards the end of the reaction when the p_H rises. This leads to a flattening or bending of the curve, indicating a slower rate of decomposition of the complex.

The values of E, the activation energy, are calculated from Fig. 4. It is found that in acid solution, the value of E is 18,650 cal./mole and in aqueous solution it is

27, 800 cal./mole. This seems to be anomalous for the same decomposition reaction occurring in acid and aqueous solutions. It may therefore be suggested that in the acid solution, the mechanism of decomposition probably differs from that in the water solution. The decomposition reaction

$$Ag^{3+} + H_2O \rightleftarrows Ag^{+} + 2H^{+} + \tfrac{1}{2} O_2 \qquad \ldots (3)$$

may be viewed as representing only the initial and final products of the reaction in both cases. But in water solution it occurs very likely through different intermediate stages, as shown below:

In water:

$$Ag^{3+} + H_2O \rightleftarrows AgO^{+} + 2H^{+}$$
$$\rightleftarrows Ag^{2+} + H^{+} + \tfrac{1}{2} H_2O_2$$
$$\rightleftarrows Ag^{+} + 2H^{+} + \tfrac{1}{2} O_2.$$

while in acid, the decomposition follows directly as given by the equation (3) above.

Fig. 6

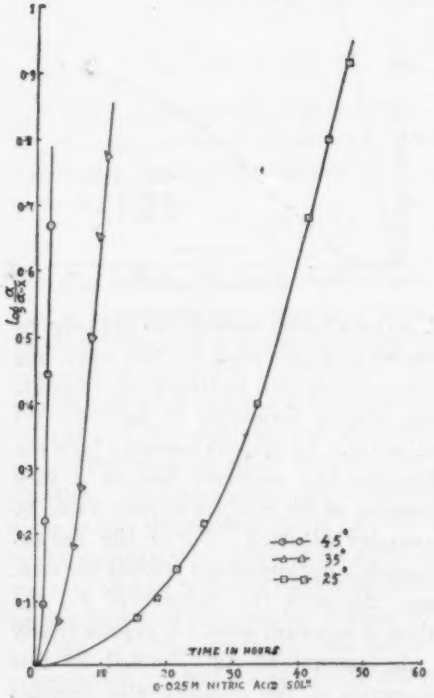
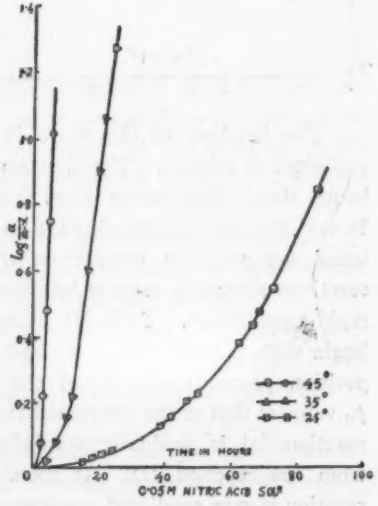


Fig. 7



The value of log A was found to be near about 9 for the acid solution and 15 for the water solution. This is in good agreement with the unimolecular reaction value.

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PREPARATION OF HEXAFLUORO-1:2-DICHLORO*cyclo*PENTENE AND A STUDY OF ITS REACTIVITY

By Kazi Abdul Latif

Preparative conditions for the preparation of *cyclo*-$C_5F_6Cl_2$ from *cyclo*-C_5Cl_8 by the action of SbF_3 containing SbF_3Cl_2, were studied and under the best condition found, a yield of 72.5% was obtained.

The structures for *cyclo*-$C_5F_4Cl_4$ and *cyclo*-$C_5F_5Cl_3$ were found to be $CCl{=}CClCF_2CFClCFCl$ and $CCl{=}CClCF_2CFClCF_2$ respectively.

A possible mechanism for the simultaneous formation of *cyclo*-$C_5F_4Cl_4$, *cyclo*-$C_5F_5Cl_3$ and *cyclo*-$C_5F_6Cl_2$ has been suggested.

Attempt was made to prepare *cyclo*-C_5F_8 from *cyclo*-$C_5F_6Cl_2$ by the action of PbO_2 and HF, but it was not successful.

Henne and Zimmerschied (*J. Amer. Chem. Soc.*, 1945, **67**, 1235) reported the preparation of hexafluoro-1:2-dichloro*cyclo*pentene (*cyclo*-$C_5F_6Cl_2$) from *cyclo*-C_5Cl_8 at a single step, by the action of SbF_3 containing 5-10% SbF_3Cl_2 and obtained a yield of 50%. *cyclo*-$C_5F_5Cl_3$ and *cyclo*-$C_5F_4Cl_4$ were also obtained as by-products. *cyclo*-$C_5F_6Cl_2$ was utilised for the preparation of hexafluoroglutaric acid by these authors and also for the preparation of hexafluoroglutarimide by Henne and Zimmer (*ibid.*, 1951, **73**, 1103). Owing to its importance as a synthetic intermediate, a re-investigation of this preparation was undertaken to find out conditions for a better yield.

The following parameters were considered : (*i*) pressure of reaction, (*ii*) relative proportion of *cyclo*-C_5Cl_8 and the fluorinating agent and (*iii*) the amount of SbF_3Cl_2 in the fluorinating mixture. Only one parameter was changed at a time, and their effect on the yield was noted.

Pressure of reaction.—While studying this, the other two parameters were as follows: the amount of flourinating agent was 3.2 moles as against one mole of *cyclo*-C_5Cl_8 used; the amount of SbF_3Cl_2 was 12%. The results obtained are shown Table I.

TABLE I

Pressure.	Yield of *cyclo*-$C_5F_6Cl_2$.	Yield of *cyclo*-$C_5F_5Cl_3$.
75 lbs.	70.05 %	7.4 %
100	72.5	1 0
150	54.8	10.7

Relative proportion of cyclo-C_5Cl_8 *and the fluorinating mixture.*—These reactions were carried out at 100 lbs. pressure using 12% catalyst. The results are shown Table II.

TABLE II

No. of moles of the fluorinating agent per mole of *cyclo*-C_5Cl_8 used.	Yield of *cyclo*-$C_5F_6Cl_2$.	Yield of *cyclo*-$C_5F_5Cl_3$.
3	69.5 %	Not recorded.
3.2	72.5	1 0 %
4	58.2	14.7

Amount of catalyst.—The effect of varying the proportion of catalyst was studied at a pressure of 100 lbs. using 3.2 moles of the fluorinating agent per mole of *cyclo*-C_5Cl_8. The results are shown in Table III.

TABLE III

SbF_3Cl_2 in the fluorinating mixture.	Yield of $C_5F_6Cl_2$.	Yield of $C_5F_5Cl_3$.
6 %	56.5 %	7.4 %
12	72.5	1.0
25	48.0	8.6

In carrying out these experiments, the reaction mixture was sealed in a steel bomb and heated overnight with steam and then heated with a free flame. Before starting the distillation, the pressure was kept constant for an hour and then distilled very slowly. This was found to be of prime importance for a good yield of *cyclo*-$C_5F_6Cl_2$ as shown by the following results.

TABLE IV

	Yield of *cyclo*-$C_5F_6Cl_2$.	Yield of *cyclo*-$C_5F_5Cl_3$.
If distilled immediately	30.5 %	30.5 %
If the pressure is kept constant for 1 hr. before distilling	72.5	1.0

One experiment was performed without steam-heating overnight, the other conditions remaining unchanged and there was found to be almost no change in the yield of *cyclo*-$C_5F_6Cl_2$.

The yield of *cyclo*-$C_5F_4Cl_4$ was always very low as found in these experiments and was almost negligible when the yield of *cyclo*-$C_5F_6Cl_2$ was high.

Structure of cyclo-$C_5F_5Cl_3$ *and* cyclo-$C_5F_4Cl_4$.—The stucture for *cyclo*-$C_5F_6Cl_2$ was established by Henne and Zimmerschied (*loc. cit.*) by its oxidation to hexafluoroglutaric acid. The structure for *cyclo*-$C_5F_4Cl_4$ was assumed by them to be

$$\overline{|\quad\quad|}$$
$$CCl=CClCF_2CCl_2CF_2$$

but no structure for *cyclo*-$C_5F_5Cl_3$ was given. In this investigation, both *cyclo*-$C_5F_4Cl_4$ and *cyclo*-$C_5F_5Cl_3$ were trearted with zinc dust and absolute ethanol. Only chlorine (and no fluorine) was pulled off form the former, while both chlorine and fluorine were pulled off form the latter. This would suggest the structure for *cyclo*-$C_5F_4Cl_4$ to be

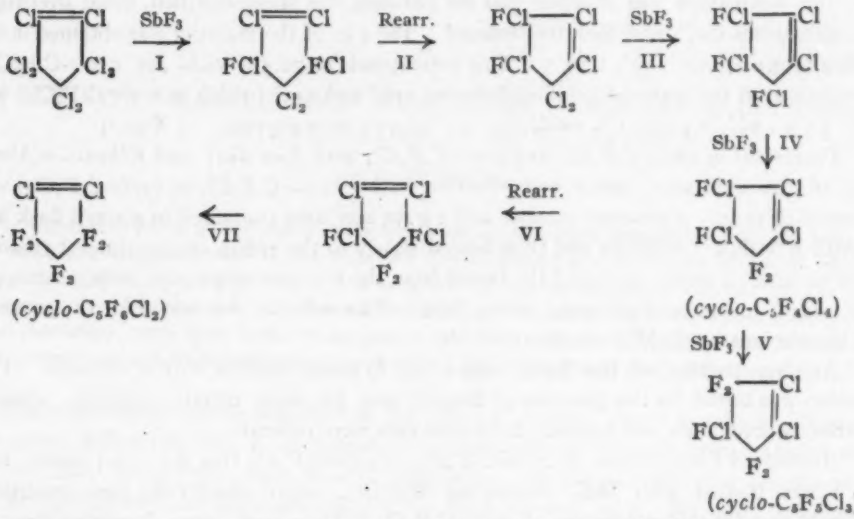
$$\overline{|\quad\quad\quad|}$$
$$CCl=CClCF_2CFClCFCl,$$

instead of the one already suggested and that for *cyclo*-$C_5F_5Cl_3$ to be either

$$\overline{|\quad\quad\quad|}\quad\quad\overline{|\quad\quad\quad|}$$
$$CCl=CClCF_2CFClCF_2 \text{ or } CCl=CClCF_2CF_2CFCl.$$

Of these two possible structures for *cyclo*-$C_5F_5Cl_3$, the former one is more likely, because that would make its conversion into *cyclo*-$C_5F_6Cl_2$ rather difficult, the -CFCl- group being flanked by two -CF_2- groups (Henne and Flannagan, *J. Amer. Chem. Soc.*, 1943, **65**, 2362). This view has been confirmed here experimentally. The structure for *cyclo*-$C_5F_4Cl_4$, as suggested here is also supported by its easy transformation to *cyclo*-$C_5F_5Cl_3$ and *cyclo*-$C_5F_6Cl_2$, as was found to be the case by Henne and Zimmerschied (*loc. cit.*).

A possible mechanism for the simultaneous formation of these fluorinated compounds from *cyclo*-C_5Cl_8 may be suggested by assuming allylic fluorination (Henne, Whaley and Stevenson, *ibid.*, 1941, **63**, 3478; Henne and Trott, *ibid.*, 1947, **69**, 1820), followed by a continuous shift of the allylic fluorine atoms:



The proposed mechanism shows that the possibility or otherwise of hexafluoride being the major product will depend on the step (V) or (VI) taking place. Probably, heating at an optimum constant pressure favours the allylic shift (step VI).

Reactivity of the Double Bond.—Henne and Zimmerschied (*loc. cit.*) reported certain amount of fluorine addition across the double bond of *cyclo*-$C_5F_6Cl_2$ by the action of SbF_5. Attempt was made in this investigation to add fluorine by the method of Henne and Waalkes (*J. Amer. Chem. Soc.*, 1945, **67**, 1639) by the action of HF and PbO_2, but it was unsuccessful.

To justify this behaviour, $CCl_2=CCl_2$, $CF_3CCl=CCl_2$ and $CF_3CCl=CClCF_3$ were treated with HF and PbO_2 under identical conditions and the results obtained showed that double bonds flanked by two $-CF_2-$ groups were almost inert under these conditions. The results are shown in Table V.

TABLE V

Compound.	n_D^{20}.	n_D^{20} of the product.	Difference.
cyclo-$C_5F_6Cl_2$	1.3670	1.3665	0.0005
$CCl_2=CCl_2$	1.5050	1.4660	0.0390
$CF_3CCl=CCl_2$	1.4040	1.3790	0.0250
$CF_3CCl=CClCF_3$	1.3455	1.3400	0.0055

EXPERIMENTAL

Preparation of cyclo-$C_5F_6Cl_2$ (*according to the best condition developed*).—*cyclo*-C_5Cl_6 (358 g., 1.03 moles), SbF_3 (519 g., 2.9 moles) and SbF_3Cl_2 (100 g., 0.4 mole) were placed into a three-litre steel bomb fitted with a steel pipe (slightly more than one inch in diameter and 4 ft. in length), and at the other end of the steel pipe were attached a pressure gauge (300 lbs) and a needle valve. The bomb was heated directly with a flame till the pressure went up to 100 lbs. where it was kept constant for one hour by regulating the heat. Distillation was then started very slowly, keeping the pressure at 100 lbs. as far as possible. The distillate was collected under ice-cold water in a receiver, which was again connected with a water scrubber. When no more distillate was coming

out, the distillation was stopped and the distillate was steam-distilled, dried overnight over anhydrous $CaCl_2$ and then fractionated ; 180.4 g. of the material was obtained in the boiling range 87°-92°, n_D^{20}, 1.3675. This corresponds to 72.5% yield for *cyclo*-$C_5F_6Cl_2$. The amount of the material distilling between 118° and 123° (which is *cyclo*-$C_5F_5Cl_3$) was only 3.0 g., n_D^{20}, 1.4045 (1% yield).

Treatment of cyclo-$C_5F_5Cl_3$ *and* cyclo-$C_5F_4Cl_4$ *with Zinc dust and Ethanol*.—About 5 ml. of the substance under consideration (either *cyclo*-$C_5F_5Cl_3$ or *cyclo*-$C_5F_4Cl_4$) was mixed with 10 ml. of absolute ethanol and 2 g. of zinc dust contained in a small flask fitted with a reflux condenser and then heated slowly to the reflux temperature of ethanol. After an hour, a small portion of the liquid from the top was taken out with a dropper and added to water containing nitric acid. This solution was tested for the presence of chloride ions by $AgNO_3$ solution.

Another portion of the liquid was added to water acidified with acetic acid. This solution was tested for the presence of fluoride ions by ceric nitrate solution, when a gelatinous precipitate was formed, if fluoride ions were present.

Attempted Fluorination of cyclo-$C_5F_5Cl_3$.—*cyclo*-$C_5F_5Cl_3$ (104.6 g., 0.4 mole, b.p. 121°) was treated with SbF_3 containing SbF_3Cl_2, under exactly the same cnnditions as found best for the preparation of *cyclo*-$C_5F_6Cl_2$. There was some decomposition, as shown by the evolution of non-condensable gases ; 45% of the starting material was recovered unchanged. Only 4.6 g. of a material boiling between 92° and 116° (n_D^{20}, 1.3810) were obtained along with 3.0 g. of another substance boiling between 121° and 152° (n_D^{20}, 1.4280). This showed that conversion to *cyclo*-$C_5F_6Cl_2$ was negligible, whereas some disproportionation producing a higher boiling material with less fluorine content in the molecule took place.

Attempted Reaction of cyclo-$C_5F_6Cl_2$ *with* PbO_2 *and* HF.—*cyclo*-$C_5F_6Cl_2$ (51 g., 0.22 mole) and PbO_2 (95.5 g., 0.33 mole) were put into a 500 ml. steel bomb and cooled in dry ice-acetone. HF (96 g., 4.1 moles), condensed from a tank, was put into the bomb and sealed with a T-joint fitted with a needle valve and a pressure gauge (reading up to 600 lbs). The bomb was then shaken mechanically till it reached a constant temperature. There was no sudden rise of pressure in this case. The bomb was then heated electrically, till the temperature reached 120°, where it was maintained for four hours. Pressure went up to 200 lbs. The bomb was then taken out of the shakar and cooled. Excess HF was allowed to pass through two bubblers containing alkali solutions. After the HF had been removed, the contents of the flask were poured into crushed ice, and cooled alkali solution was added. It was then steam-distilled and dried ; 36.1 g. of the material were obtained having n_D^{20}, 1.3665 ; recovery was 74%. Evidently there was some loss in handling.

The work was carried out at the Organic Chemistry Laboratory of the Ohio State University, Columbus, Ohio, U.S.A. The author is very much indebted to Prof. Albert L. Henne of that department for many helpful suggestions. Thanks are also due to the Institute of International Education, New York, for arranging a Fellowship which enabled the author to work there.

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ION ACTIVITY MEASUREMENTS WITH RESIN MEMBRANE ELECTRODES. PART I. DETERMINATION OF MONOVALENT IONS

By S. K. Sinha

The activities of Na, K and H ions in electrolytic solutions have been determined with the help of resin membrane electrodes used in the form of a thin membrane, moulded from a mixture of various cation-exchanging resins and polystyrene. The suitability of the various resins for this purpose has been discussed and two resins, one a commercial resin Ionac C-200, and the other, RF-resin, prepared in this laboratory, have been found to be more suitable than others. The range of concentrations to which measurement of activity is possible is much higher than in the case of clay membranes.

The measurement of the activities of Na^+, K, Ca^+ or Mg^+ ions is no doubt attended with great difficulties but is of considerable importance to the soil chemist (Marshall, *Soil Sci. Soc. Amer. Proc.*, 1944, **8**, 175; MacLean, *ibid.*, 1949, **14**), the physiologist and the biochemist (Carr and Leotopol, *J. Phys. Coll. Chem.*, 1950, **54**, 176; Scatchard and Black, *ibid.*, 1949, **53**, 88; Fenn, *Physiol. Rev.*, 1936, **16**, 450).

Marshall and his co-workers have successfully used clay membranes for the determination of sodium (Marshall and Krinbill, *J. Amer. Chem. Soc.*, 1942, **64**, 1814), potassium (Marshall and Bergman, *ibid.*, 1941, **63**, 1911), ammonium (Marshall and Bergman, *J. Phys. Chem.*, 1942, **46**, 325), calcium (Marshall and Ayers, *Soil Sci. Amer. Proc.*, 1946, **11**, 117), magnesium (Marshall and Eime, *J. Amer. Chem. Soc.*, 1948, **70**, 1302) and barium (Marshall and Chatterjee, *J. Phys. Coll. Chem.*, 1950, **54**, 671) ions in electrolytic solutions as well as clay suspensions. Sollner with other co-workers has developed collodion membranes for the measurements of activities of both cations (*J. Amer. Chem. Soc.*, 1943, **65**, 2260; Gregor, Ph.D. Thesis, University of Minnesota, 1945) as well as anions (Abrams and Sollner, *J. Phys. Chem.*, 1946, **50**, 53) in electrolytic solutions.

The success of Marshall and his co-workers in the field of clay membranes led Wyllie and Patnode (*J. Phys. Coll. Chem.*, 1950, **54**, 204) to use a synthetic ion-exchange risin for the measurement of the activities of sodium ions in concentrated solutions. The present author, in this and in subsequent papers to be published, has used a number of cation exchangers in the form of a thin membrane, as electrodes for the measurements of the activities of sodium, potassium, hydrogen, calcium and magnesium ions, and anion exchangers for the determination of chloride and sulphate ions.

Experimental

The present work was carried out with the following types of resins.

1. Amberlite IR-100 is a phenolic methylene sulphonic acid resin with a total exchange capacity of 1.75 m.e./g., prepared by Messrs. Rohm and Haas Co., Philadelphia. It was obtained in the H-form.

2. Ionac C-200 is also a phenolic methylene sulphonic acid resin with an exchange capacity of 2.70 m.e./g., prepared by the American Cyanamid Co., N. Y. It was obtained in the Na-form.

3. Amberlite IR-120 is a nuclear sulphonic acid resin with a total exchange capacity of 4.2 m.e./g., prepared by Messrs. Rohm and Haas Co., Philadelphia.

4. Amberlite IRC-50 is a carboxylic acid resin with an exchange capacity of 10.0 m. e./g., prepared by Messrs. Rohm and Haas Co.

5. Resorcylic acid-formaldehyde resin. *β*-Resorcylic acid (5 g.), prepared by the method of Hickinbottom ("Reactions of Organic Compounds", 1948), was dissolved in the least quantity of dilute alkali solution and heated on a water-bath. Then 20 c.c. of 40% formaldehyde and 2 c.c. of concentrated NaOH solution were added. After heating for some time beautiful amber-coloured resin was formed, which was heated on the water-bath for about 4 hours. The mass shrank in bulk and the colour changed to shining black. It was washed with water and finally with dilute sodium carbonate solution, and then cured in an air-oven at 90°. The granular resin thus obtained was in the Na-form.

6. Hydroxybenzoic acid-formaldehyde resin was prepared in the following manner. *m*-Hydroxybenzoic acid (5 g. appox.) and salicylic acid (5 g.) were dissolved in 3 g. of NaOH (satd. soln.). 40% Formaldehyde (15 c.c.) was added, and the mixture heated on a water-bath for about half an hour, then acidified with HCl (conc.). A gum-like white resin was formed which was freed from the adhering water and heated at 120° for 4 hours. A glassy mass was obtained. It was brittle at ordinary temperature and broke with a fracture. The mass absorbed moisture on standing and became plastic on heating to 80°. It was powdered and soaked in dilute sodium carbonate solution, finally washed and dried. The resin, thus obtained in the Na-form, is slightly reddish brown.

Polystyrene was used as a binder in the preparation of the membranes. As finely powdered polystyrene was not available to us, ordinary granular polystyrene of the market was treated in the following manner to get it in the required fineness. Polystyrene was dissolved in benzene and sprayed into a glass chamber where it was deposited on evaporation of benzene, in the form of a soft fibrous mass. This was collected and gently rubbed over the proper sieve when they passed through it in the form of a fine powder. The granular polystyrene, as it is, could not be ground fine by the usual mechanical means.

Technique of Measurement.—The technique of measurement of E. M.F. was basically the same as evolved by Marshall and his co-workers in the field of clay membranes.

The resin membranes suitable for this purpose were prepared under hydraulic press in a steel mould from a mixture of the finely powdered ($<$ 200 mesh U.S. standard) exchange resin usually with a similarly powdered polystyrene. The temperature of the mould was adjusted according to the resins used and varied from 90° to 140° The pressure was usually maintained at 4000 lbs. p. s. i. for about a quarter of an hour till the system cooled to 80°—90°. The melted mixture formed a coherent membrane in which the exchange resin was uniformly distributed in the matrix of the binder resin. The thickness, depending upon the quantity of the mixture, varied from 0.2 to 0.5 mm.

The membranes were cut into suitable sizes and fixed to one of the ends of a pyrex glass tubing, about 8 to 10 mm. in diameter, with the help of a commercial adhesive "Durofix", prepared by Messrs. Rawlplug Ltd., London. The membrane electrodes, thus prepared, were soaked both inside and outside for about 72 hours or even more in a concentrated solution of the salt containing the ion whose activity it was desired to measure. The membranes were first tested for asymmetry potentials, if any. For this purpose, dilute solutions of the same electrolyte having equal activities were placed on both sides of the membrane. Electrical connections between the two sides were made by dipping into the solutions tiny saturated calomel electrodes having KCl-agar tips. The membranes showing in this way absence or negligible asymmetry potentials were used for further measurements. The E.M.F.'s were read within ± 0.1mv. with the help of L & N-K_2 type potentiometer and a Hartmann and Braun galvanometer having a current sensitivity of 10^{-10} amps. mm./m. For reproducible results it was often necessary to change the salt solutions two or three times on both sides of the membrane. The electrical resistances of the membranes, which were more or less constantly used in the present investigation, are shown in Table I.

TABLE I

Membranes used.	Thickness of membranes.	Total resistance.
Amberlite IR—100	0.6 mm.	0.5 megohms
Ionac C—200	0.5	0.6
Amberlite IR C—50	0.6	0.6
*RF—resin	0.5	0.75
*MF resin	0.4	0.8
Amberlite IR—120	0.5	0.2

*RF stands for resorcylic acid-formaldehyde resin and MF for *m*-hydroxybenzoic acid-formaldehyde resin.

When not in use, the membranes kept well if soaked in about 0.1*N* salt solutions.

Measurement of the electrical resistance of the membranes in different salt solutions and also in different concentrations of the same salt showed that it was almost independent of the nature and concentration of the salts, provided that the solutions were not too dilute.

Effect of Thickness.—It was observed in agreement with Wyllie and Patnode (*loc. cit.*) that if the membranes were very thin and less than 0.2 mm., the observed potential was low and in case they were very thick, the resistances were too high for very accurate E.M.F. measurements. The thickness was best maintained between 0.2 and 0.5 mm. by adjusting the total quantity of the resin and binder mixture in the mould.

Effect of varying the Percentage of Exchange Resin in the Membrane.—An increase in the proportion of the exchange resin was found to decrease the electrical resistance of the membranes and also the time for attainment of equilibrium. But by increasing the % resin above 70%, which was generally the optimum percentage, the mechanical strength of the membranes was considerably reduced. In some cases the % resin had to be lowered. In the preparation of these membranes about 50% resin was used to counteract the effect due to swelling of the resins, as in the case of Amberlite IR-120 and Amberlite IRC-50.

Effect of Pressure employed in the Preparation of the Membranes on their Properties.—No marked effect on the membrane properties was observed by using different moulding pressures, except that the membranes moulded at high pressures showed better surfaces, had less asymmetry potentials and a slightly lower electrical resistance. A pressure of 4000 lbs. p.s.i. was found to be quite suitable, and this was employed in the preparation of all the membranes used in this investigation.

Preparation of Standard Solutions.—For the purpose of studying the behaviour of the membranes towards various ions, a series of salt solutions was so prepared that the ratio of the ion activities for successive pairs was either 3:1 or 10:1.

The calculations of ionic activity coefficients are based on the assumptions that, (1) in KCl solutions the activity coefficients of K^+ and Cl^- ions are equal and (2) in any other chloride solution of the same ionic strength, the choride-ion activities are equal. The activities of sodium (Harned and Nims, *J. Amer.Chem.Soc.*, 1932, **54**, 423) and potassium (Harned and Cook, *ibid.*, 1937, **59**, 1290) ions were calculated from the mean activity coefficients compiled from the works referred to against each.

Reproducibility of Measurements.—For each measurement at least three different membranes of the same resin, prepared under identical conditions, were used. The mean value of the equilibrium potentials was recorded. In order to eliminate any asymmetry potentials, E.M F. measurements were also made by interchanging the inside and outside solutions. Using membranes having desirable properties, viz., good electrical conductance, absence of swelling and a smooth polished surface and optimum thickness, the same E.M.F. values were obtained over the period of two years the author had worked with them.

Measurement of Sodium-ion Activity.—The E.M.F.s were measured by interposing different membranes between sodium chloride solutions of known ion activities. The theoretical value of the E.M.F. was calculated, using the Nernst equation and compared with the experimental values. The results of measurement with six different types of membrane electrodes over a wide range of sodium-ion activities are shown in Table II.

TABLE II

Conc. of electrolytes C_2: C_1 in g. mols. per 1000 g. H_2O.	Experimental E. M. F. in mv. using Amberlite IR-100.	Inoac C-200.	RF-resin.	Amberlite IR-120.	Amberlite IRC-50.	MF-resin.	Theoretical E.M.F. in mv.
0.0097/0.00103	58.1	56.2	55.6	55.5	53.6	57.2	56.2
0.0308/0.0031	57.2	56.2	56.0	51.8	55 6	54.4	,,
0.1000/0.107	56.2	56.2	56.5	48.0	49.8	42.2	,,
0.3295/0.0308	55.4	56.2	56.0	44.6	50.6	37.2	,,
1.0000/0.107	51.2	51.3	47.5	42.2	38.4	31.6	55.0
2.0000/0.25	42.8	46.0	41.8	41.0	—	—	,,
4.0000/0.7000	29.2	36.6	30.0	24.0	—	—	,,

Measurement of Sodium-ion Activity in Sodium Sulphate Solutions.—Marshall (*J. Amer. Chem. Soc.*, 1941, **63**, 1911) has observed that anions affect very little the cation activities of electrolytic solutions as measured by clay membranes. The performance of the resin membrane electrodes in this respect is shown by the following measurements made with sodium sulphate solution on one side and sodium chloride on

the other side of the membrane. The sodium-ion activities, calculated from the observed E.M.F.'s, are compared with the theoretical values (Lewis and Randall, "Thermodynamics"). The results are embodied in Table III.

TABLE III

Ion activities of electrolytes used.		a_{Na^+} experimental, using		
Inner soln. (NaCl) a_{Na^+}	Outer soln. (Na_2SO_4) $a_{SO_4^-}$	Ionac C-200.	RF resin.	a_{N^+} (Theor.).
0.00877	0.01514	0.0862	0.0768	0.1040
,,	0.00505	0.0193	0.0181	0.0210
,,	0.00168	0.0049	0.0043	0.0055
,,	0.00056	0.0016	0.0012	0.0018

In view of the assumptions involved in the calculations of ion activities the agreement appears to be fairly satisfactory, especially in the more dilute solutions and suggests that sulphate ions in the range studied have no appreciable effect on the performance of the resin membrane electrodes, so far as the measurement of sodium-ion activities is concerned.

Measurement of Potassium-ion Activities.—Potassium-ion activities in potassium chloride solutions were measured in the same way as sodium-ion activities, but a lower range of concentration was covered. The results are shown in Table IV.

TABLE IV

Measurements of a_{K^+} in KCl solutions.

Conc. of electrolytes C_2: C_1 in g. mols./ 100.g. H_2O.	Mean experimental E. M. F in mv., using						Theoretical E.M.F. in mv.
	Amberlite IR-100.	Ionac C-200.	RF-resin.	Amberlite IR-120.	Amberlite IRC-50.	MF-resin.	
0.003/0.001	27.6	28.2	28.2	28.2	26.6	29.0	28.1
0.0098/0.0030	28.2	29.5	28.4	27.5	28.2	28.5	,,
0.0300/0.0098	28.2	28.7	28.2	26.6	25.0	21.0	,,
0.102/0.03	28.6	28.7	28.0	24.1	25.5	19.0	,,
0.35/0.102	28.4	28.0	27.1	24.8	19.0	16.0	,,

The performance of the resin IR-100, C-200 and RF, as can be seen from the above data, is very satisfactory within the range of concentrations studied. The others perform well in the more dilute solutions.

Hydrogen-ion Activity.—Two of the resin membranes studied above have been used to measure the hydrogen-ion activities of pure acid solutions *i.e.*, in the absence of other cations. Table V gives the results of measurements in pure hydrochloric acid solutions and the experimental values of the activities were compared with those calculated on the basis of p_H measurements with a Muirhead p_H-meter using glass electrode.

TABLE V

Ratio of activities using glass electrode.	Experimental E.M.F. in mv. using		Theoretical E.M.F. in mv. calc. from glass electrode data.
	Ionac C-200.	RF-resin.	
0.0013/0.00045	28.2	28.2	26.3
0.0044/0.0013	28.2	28.3	31.3
0.0126/0.0044	27.5	27.5	27.3
0.0350/0.0126	26.8	26.8	26.3

The above results suggest a useful application of resin membrane electrodes to p_H measurements, especially in the absence of other cations. They therefore serve, at least partly, the purpose of glass electrodes. These resin membranes are, however, from the point of view of preparation and manipulation more convenient than glass electrodes. A further usefulness of the resin membrane electrode is to be found in the potentiometric titrations carried out with them (to be published in a subsequent paper).

DISCUSSION

Amongst the various resins used in the measurements of the activities of monovalent cations, Ionac C-200 and RF-resin seem to give the best results. The resistance is low and the final equilibrium is attained within 5 to 10 minutes.

For concentrated solutions of sodium chloride the measured E.M.F.'s are much below the theoretical values. The three series of membranes of Ionac C-200 and Amberlite IR-100, prepared at different times, give almost the same results. It may, however, be mentioned here that the values of the E.M.F.'s at higher concentrations, although lower than the theoretical value, are reproducible and constant for membranes of any particular resin. The range of validity of the Nernest equation in sodium chloride solutions is graphically illustrated in Fig. 1, where the observed E.M.F.'s are plotted against log $1/C$ for solution pairs having definite C_1/C_2 ratio.

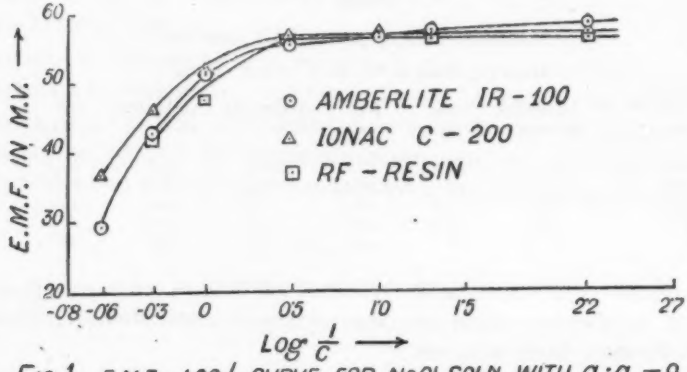

FIG. 1. E.M.F. $-\log \frac{1}{C}$ CURVE FOR NaCl SOL$^{N}_{2}$ WITH $a_1 : a_2 = 9$

The author's thanks are due to Dr. S. K. Mukherjee of the University College of Science for his helpful suggestions and keen interest, and to Dr. P. C. Rakshit, Head of the Dept. of Chemistry, Presidency College, for providing laboratory facilities. Thanks are also due to the American Cyanamid Co., and to Messrs. Rohm and Haas Co., Philadelphia, for making available free samples of some of the resins used in course of this work.

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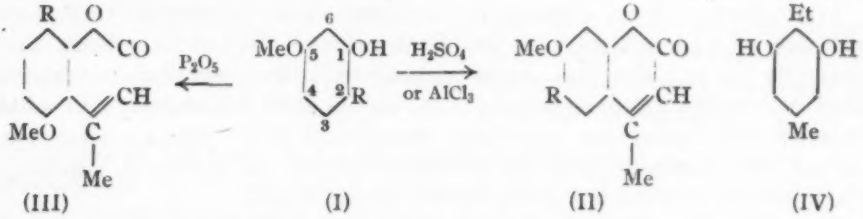
PECHMANN CONDENSATION. PART I. CONDENSATION OF 2:5-DISUBSTITUTED PHENOLS WITH ETHYL ACETOACETATE

By R. N. Usgaonkar, V. M. Thakor and G. V. Jadhav

2-Ethyl- and 2-propyl-5-methoxyphenols on condensation with ethyl acetoacetate in presence of aluminium chloride or sulphuric acid gave 6-ethyl- and 6-propyl-7-methoxycoumarins respectively, the alkyl groups having migrated. However, when the condensation of the former was effected in presence of phosphorus pentoxide, 5-methoxy-4-methyl-8-ethylcoumarin was obtained. 2-Ethyl-5-methylresorcinol similarly gave 7-hydroxy-4:5-dimethyl-8-ethylcoumarin, in presence of sulphuric acid, aluminium chloride or phosphorus pentoxide.

Pechmann condensation of 2 alkyl-5-alkoxyphenols with ethyl acetoacetate in presence of sulphuric acid, aluminium chloride and phosphorus pentoxide has been investigated.

2-Ethyl-5-methoxyphenol (I, R = Et) condensed with ethyl acetoacetate in presence of anhydrous aluminium chloride or 80% sulphuric acid. The product obtained was identified as 7-methoxy-4-methyl-6-ethylcoumarin (II, R = Et) and not the expected 5-methoxy-4-methyl-8-ethylcoumarin (III, R = Et), the alkyl group having migrated from 2 to 4 position (I). This constitution was assigned to the product because on demethylation it gave the known 7-hydroxy-4-methyl-6-ethylcoumarin. However, when the condensation was effected in presence of phosphorus pentoxide, 5-methoxy-4-methyl-8-ethylcoumarin (III, R = Et) was obtained.



(III) (I) (II) (IV)

2-Propyl-5-methoxyphenol (I, R = *n*-Pr) similarly gave 7-methoxy-4-methyl-6-propylcoumarin (II, R = *n*-Pr) in presence of sulphuric acid or aluminium chloride. These are the first instances where migration during Pechmann condensation has been observed.

In view of the results obtained in the present work, and in subsequent works*, it was considered worthwhile to reinvestigate the Pechmann condensation of 2-ethyl-5-methylresorcinol (IV). In presence of sulphuric acid, as observed by Desai and Mavani (*Proc. Ind. Acad. Sci.*, 1947, **15A**, 341), 7-hydroxy-4:5-dimethyl-8-ethylcoumarin was obtained. The same product was obtained when either phosphorus pentoxide or anhydrous aluminium chloride was used. The constitution was established by converting the coumarin into the methoxycinnamic acid derivative.

*To be published in the next issue.

The results are interesting as different products are obtained in presence of sulphuric acid or aluminium chloride on the one hand, and phosphorus pentoxide on the other. However, the yields obtained are low, and it would be premature to draw any conclusion at this stage. Further work is in progress.

EXPERIMENTAL

2-Ethyl-5-methoxyphenol (I, R=Et).—It was prepared by the Clemmensen's reduction of phenol (45 g.) with zinc amalgam (from 100 g. of zinc dust) and hydrochloric acid (1 : 1, 700 c.c.), by refluxing for 6 to 7 hours. The oil separating on cooling was taken up in ether, dried and the ether removed. The residual oil, when distilled under reduced pressure, came at 158°-160°/23 mm. as colorless oil (30-35 g.). (Found : C, 70.5 ; H, 7.9. $C_9H_{12}O_2$ requires C, 70.1 ; H, 7.9 per cent).

Condensation of 2-Ethyl-5-methoxyphenol (I, R=Et) *with Ethyl Acetoacetate : 7-Methoxy-4-methyl-6-ethylcoumarin* (II, R=Et)

In presence of Anhydrous Aluminium Chloride.—2-Ethyl-5-methoxyphenol (5.0 g.) and ethyl acetoacetate (5.0 g.) were treated with anhydrous aluminium chloride (9.0 g.) in nitrobenzene (50 c.c.) and the reaction mixture heated on a steam-bath for 3 hours. It was cooled, ice and hydrochloric acid were added and the nitrobenzene was removed by steam distillation. The residual black solid was crystallised from dilute alcohol (charcoal) two or three times when finally colorless tiny needles of 7-methoxy-4-methyl-6-ethylcoumarin (II, R=Et), m.p. 162-63°, were obtained. (Found : C,71.1 ; H, 6.7. Calc. for $C_{13}H_{14}O_3$: C, 71.1 ; H, 6.4 per cent). Desai and Ekhlas (*Proc. Ind. Acad. Sci.*, 1938, **8A**, 197) give m.p. 160°.

In presence of 80% Sulphuric Acid.—A mixture of the phenol (5.0 g.), ethyl acetoacetate (5.0 g.) and sulphuric acid (80%, 40 c.c.) was kept for 20 hours at room temperature (*ca.* 30°) and then poured crushed ice. The pasty mass obtained was treated with sodium hydroxide solution (10%) and the solid, thus obtained after washing thoroughly with water, was crystallised from alcohol (60%), when a product of m.p. 130-°145° was obtained. After several crystallisations, fine needles of 7-methoxy-4-methylcoumarin (m.p. and mixed m.p., 161-63°) were obtained.

The methoxycoumarin (1.0 g.) was demethylated with hydriodic acid (10 c.c.) in acetic anhydride (12 c.c.) by heating at 140°-145° for 3 hours. It was worked up as usual and crystallised from alcohol (95%) when 7-hydroxy-4-methyl-6-ethylcoumarin (m.p. and mixed m.p., 213-14°) was obtained. Desai and Ekhlas (*loc. cit.*) give m.p. 213°.

Condensation of 2-Ethyl-5-methoxyphenol (I, R=Et) *with Ethyl Acetoacetate in presence of Phosphorus Pentoxide : 5-Methoxy-4-methyl-8-ethylcoumarin* (III, R=Et)

To a mixture of the phenol (6.0 g.) and ethyl acetoacetate (5.4 g.), phosphorus pentoxide (8.0 g.) was slowly added with cooling. Vigorous reaction occurred with evolution of heat. It was kept in ice for half an hour, more oxide (8.0 g.) was added and the reaction mixture heated on a water-bath at 60°-80° for about half an hour. It was cooled, water added and basified with dilute sodium hydroxide solution. The product obtained was treated with sodium hydroxide solution and extracted with ether.

The extract was washed and dried, and the ether removed. The pasty mass was treated with a little rectified spirit at 0° when 5-methoxy-4-methyl-8-ethylcoumarin (III, R=Et) separated as a crystalline solid. It was collected, washed and crystallised from dilute alcohol in colorless plates, m.p. and mixed m.p. 106°-107°. Sethna and Shah (*J. Chem. Soc.*, 1938, 1068) give m.p. 107°-109°.

The methoxycoumarin (0.5 g.) was demethylated with hydriodic acid (4 c.c.) and acetic anhydride (5 c.c.) as in the previous case when 5-hydroxy-4-methyl-8-ethylcoumarin, m.p. 211-12°, was obtained. Sethna and Shah (*loc. cit.*) give m.p. 212-13°.

2-Propyl-5-methoxyphenol (I, R = Pr).—Respropiophenone monomethyl ether (40 g.), zinc amalgam (from 100 g. of zinc dust) and hydrochloric acid (1:1, 700 c.c.) were refluxed for 6 to 7 hours. The oil separating solidified on cooling (0°). It was extracted with ether, dried and the ether removed. 2-Propyl-5-methoxyphenol obtained distilled at 160°-162°/14 mm. as colorless oil which immediately solidified, m.p. 39-40°. (Found: C, 72.2 ; H, 8.4. $C_{10}H_{14}O_2$ requires C, 72.3; H, 8.4 per cent).

Condensation of 2-Propyl-5-methoxyphenol (I, R=Pr) *with Ethyl Acetoacetate: 7-Methoxy-4-methyl-6-propylcoumarin* (II, R=Pr)

In presence of Anhydrous Aluminium Chloride.—The phenol (5.0 g.), ethyl acetoacetate (4.5 g.) and anhydrous aluminium chloride (9.0 g.) in dry nitrobenzene (40 c.c.) were heated on a steam-bath for 3 hours. It was cooled, ice and hydrochloric acid added and the nitrobenzene removed by distillation with steam. The dark residue was crystallised three times from 95% alcohol (charcoal) when 7-methoxy-4-methyl-6-propylcoumarin separated in colorless long needles, m.p. 172-73°. (Found: C, 72.5; H, 7.0. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9 per cent). It did not depress the melting point of the methyl ether of 7-hydroxy-4-methyl-6-propylcoumarin, prepared from the coumarin (1 g.), dimethyl sulphate (0.7 g.) in acetone and sodium hydroxide solution.

In presence of Sulphuric Acid.—The phenol (5.0 g.), ethyl acetoacetate (4.5 g.) and sulphuric acid (30 c.c.) were mixed and kept at room temperature (*ca.* 30°) for 20 hours, and poured over crushed ice. The product separating was washed with sodium hydroxide solution (10%), then with water and crystallised from alcohol when a product of m.p. 135°-145° was obtained. After several crystallisations it gave the above methoxycoumarin, m.p. 172-73°.

On demethylation of the methoxycoumarin (1.0 g.) with hydriodic acid (8.c.c.) in acetic anhydride (10 c.c.) at 140°-150° for 3 hours, 7-hydroxy-4-methyl-6-propylcoumarin (m.p. and mixed m.p. 178-79°) was obtained. (Found: C, 71.0, H, 6.7. Calc. for $C_{13}H_{14}O_3$: C, 71.5; H, 6.4 per cent). Chakravarti and Chakravarti (this *Journal*, 1939, **16**, 149) give m.p., 174-75°. The *acetyl* derivative prepared from the coumarin (0.7 g.) with acetic anhydride (10 c.c.) and pyridine was crystallised from alcohol (95%) in colorless needles, m.p. 114-15°. (Found: C, 69.0; H, 6.7. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.2 per cent).

Condensation of 2-Propyl-5-hydroxyphenol (4-Propylresorcinol) with Ethyl Acetoacetate in presence of Phosphorus Oxychloride: 7-Hydroxy-4-methyl-6-propylcoumarin

4-Propylresorcinol (2.0 g.), ethyl acetoacetate (2.0 g.) and phosphorus oxychloride (1 c.c.) were mixed when a vigorous reaction occurred. It was kept for 20 hours at room temperature, digested with water and the solid collected, washed and crystallised from alcohol in colorless prisms, m.p. 178-79°.

Condensation of 2-Ethyl-5-methylresorcinol (γ-Ethylorcinol) (IV) with Ethyl Acetoacetate: 7-Hydroxy-4:5-dimethyl-8-ethylcoumarin

In presence of Anhydrous Aluminium Chloride.—The phenol (1.0 g.), ethyl acetoacetate (1.0 g.) and anhydrous aluminium chloride (1.8 g.) in dry nitrobenzene (7.0 c.c.) were heated at 120°-125° in an oil-bath for 2 hours. It was cooled, ice and hydrochloric acid added and the nitrobenzene removed as usual. The residue on crystallisation from alcohol gave 7-hydroxy-4:5-dimethyl-8-ethylcoumarin as colorless prisms, m.p. 241-42°. Desai and Mavani (*Proc. Ind. Acad. Sci.*, 1947, **15A**, 341) give m.p. 235°.

In presence of Phosphorus Pentoxide.—The phenol (1.0 g.), ethyl acetoacetate (1.0 g.) and phoshporus pentoxide (2.0 g.) were heated on a steam-bath for an hour, more oxide (2.0 g.) added and heated for another hour. It was digested with water, and the solid that separated was collected, washed and crystallised when the above coumarin, m.p. 241-42°, was obtained.

The same coumarin was obtained when the condensation was carried out in presence of sulphuric acid (80%) according to the conditions of Desai and Mavani (*loc. cit.*).

2:4-Dimethoxy-3-ethyl-β-6-dimethylcinnamic Acid.—The above coumarin (0 5 g.), dimethyl sulphate (2 c.c.), sodium hydroxide solution (10%, 15 c.c.) and acetone (5 c.c.) were refluxed and more dimethyl sulphate (6 c.c. in all) and sodium hydroxide solution (10%, 50 c.c.) were added in small amounts, the heating being carried out for an hour. It was cooled, filtered and the filtrate acidified. The acidified solution was extracted with ether, and the extract washed with sodium bicarbonate solution. The bicarbonate extract was neutralised and shaken with ether. The ethereal layer after drying and removal of the ether furnished an oil which slowly solidified It was crystallised from dilute alcohol when the methoxycinnamic acid derivative separated in colorless needles, m.p. 138-40°. (Found : C, 68.0; H, 7.4. $C_{15}H_{20}O_4$ requires C, 68.2; H, 7.5 per cent).

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A NEW SYNTHESIS OF *p*-NITROBENZENE SULPHONYL CHLORIDE

By K. Raman and M. Raghavan

A new method of synthesis of *p*-nitrobenzene sulphonyl chloride has been described. Though methods of preparation of this compound are known, its purification is very tedious and the yields are low. The new method obviates all these difficulties as the pure compound is obtained at the end of the reaction.

p-Nitrobenzene sulphonyl chloride is a valuable intermediate in the preparation of some of the important sulpha drugs, and is particularly employed in the manufacture of sulphanilamide derivatives which are sensitive to strong acids or alkalies. If in the synthesis of such sulphanilamide derivatives, *p*-acetaminobenzene sulphonyl chloride (N-acetylsulphanilyl chloride) is used as an intermediate, it has been observed that subsequent hydrolysis of the resulting acetaminosulphanilamide derivatives to the corresponding amino compounds is accompanied by the decomposition of the amino-sulphanilamide derivatives. Further, the nitro group of *p*-nitrobenzene sulphonyl chloride confers increased acidity on the compound, and as such it finds a special application in the manufacture of sulphanilamide derivatives derived from weak amines.

The nitro group of the sulphanilamide derivatives, prepared by employing *p*-nitrobenzene sulphonyl chloride may be reduced to the amino group under nearly neutral conditions. To cite a few examples, the manufacture of sulphapyridine, sulphaguanidine, sulphadiazine, sulphamerazine and sulphamethazine, is carried out using *p*-nitrobenzene sulphonyl chloride as an intermediate.

There are a number of methods mentioned in literature (Obermiller, *J. prakt. Chem.*, 1914, *ii*, **89**, 84, ; Ekbom, *Ber.*, 1902, **35**, 653 ; Blanksma, *Rec. trav. chim.*, 1901, **20**, 129; Alber, *J. Franklin Inst.*, 1939, **228**, 127 ; Witte, *Rec. trav. chim.*, 1932, **51**, 299 ; Bell, *J. Chem. Soc.*, 1928, 2770) for the preparation of *p*-nitrobenzene sulphonyl chloride, out of a which that due to Barber (*J. Chem. Soc.*, 1943, 101) wherein the *pp'*-dinitrodiphenyl disulphide, obtained by the action of sodium disulphide on *p*-nitrochlorobenzene, is oxidised and chlorinated simultaneously by passing chlorine through a suspension of the compound in acetic acid, is a somewhat satisfactory one. But the sulphonyl chloride obtained by this method is not pure as it contains more than 20% of *bis*(*p*-nitrophenyl)sulphoxide and considerable amounts of *bis*(*p*-nitrophenyl)-sulphone in addition to other impurities. These impurities offer great difficulties when purification of the sulphonyl chloride is attempted. Complete purification could not be effected by crystallisation. Partial purification with considerable loss of the sulphonyl chloride is alone possible from solvents like ethylene dichloride, trichloroethylene, glacial acetic acid or mixtures of these. The pure product can be obtained by vacuum distillation at 1-2 mm. pressure, but this procedure involves the risk of explosion at the early stages of the distillation, in nine out of ten cases, even if carried out

with utmost care. This is attributed to the presence of *p*-nitrobenzene sulphonyl chloride occluded in the sulphonyl chloride and arising through the incomplete oxidation at the chlorination stage.

A new method of synthesis of *p*-nitrobenzene sulphonyl chloride, which obviates all the aforementioned difficulties and yields the pure compound, has been carried out following the steps shown below :

$$\underset{\text{(I)}}{p\text{-}HO_3S.C_6H_4.NH_2} \xrightarrow[NaNO_2+HNO_3]{\text{Diazotisation}} \underset{\text{(II)}}{\text{Diazo salt}} \xrightarrow[Cu_2O+HNO_3]{\text{Replacement of the diazo group}} \text{(III)}$$

$$\underset{\text{(III)}}{HO_3S.C_6H_4.NO_2} \xrightarrow[\text{Neutralisation with KOH soln. and evaporation to dryness}]{\text{Preparation of K-salt}} \underset{\text{(IV)}}{p\text{-}KO_3S.C_6H_4.NO_2}$$

$$\text{(IV)} \xrightarrow[\text{(2) with } Cl.SO_3H]{\text{Formation of acid chloride (1) with } PCl_5} \underset{\text{(V)}}{p\text{-}O_2N.C_6H_4.SO_2Cl}$$

According to the new method, *p*-nitrobenzene sulphonyl chloride was prepared starting from sulphanilic acid, a cheap and readily available organic intermediate.

Sulphanilic acid was diazotised and the diazonium salt treated with cuprous oxide and dilute nitric acid in order to replace the diazonium group by nitro group. The resulting *p*-nitrobenzene sulphonic acid was converted into the potassium salt. The dry potassium salt on treatment with phosphorus pentachloride gave *p*-nitrobenzene sulphonyl chloride, m.p. 78-79°.

The conversion of the diazonium salt of sulphanilic acid to *p*-nitrobenzene sulphonic acid was carried out either by separation of the solid diazo salt from the diazonium salt mixture and subsequent treatment of the separated diazo salt with dilute nitric acid and cuprous oxide or by treating the diazonium salt mixture as such without isolation of the diazo salt, with dilute nitric acid and cuprous oxide. The yield of *p*-nitrobenzene sulphonic acid, as judged by the quantity of sulphonyl chloride obtained therefrom, is almost the same in the case of the two types of experiments outlined (*vide supra*).

Several experiments were conducted to standardise the procedure for converting the crude potassium *p*-nitrobenzene sulphonate to the corresponding sulphonyl chloride using either phosphorus pentachloride or chlorosulphonic acid. All these are embodied in the accompanying table.

The yields of *p*-nitrobenzene sulphonyl chloride obtained, while using chlorosulphonic acid, are not appreciable. In the case of experiments wherein phosphorus pentachloride was used, the yield of *p*-nitrobenzene sulphonyl chloride varied from 27-59% depending on the experimental conditions. Good yields of *p*-nitrobenzene sulphonyl chloride were obtained in experiments 8-11.

The sulphonyl chloride was further characterised through its amide. *p*-Nitrobenzene sulphonyl chloride, when made according to this method, was not contaminated with any other impurities.

TABLE I

Preparation of p-*nitrobenzene sulphonyl chloride from potassium* p-*nitrobenzene sulphonate.*

Expt. No.	Crude K salt.	PCl_5.	Temp.	Duration of heating.	Yield.	% Calculated on sulphanilic acid.
1	10 g.	4 g.	20-25°	1 hour	Very little	
2	10	4	60°	1 ,,	,,	
3	10	4	using a solvent, $CHCl_3$ (20 c c.) at 20-25°	1 hr.	Not appreciable	
4	10	10	60-70°	15 min.	0.84 g.	27
5	10	10	60°	1 hr.	0.9	29
6	10	20	40-60°	1 ,,	1.1	36
7	10	20	60°	45 min.	1.5	49
8	10	20	60°	1 hr.	1.6	52
9	10	20	60°	1 ,,	1.66	54
10	10	20	60°	1 ,,	1.72	56
11	10	20	60°	1 ,,	1.80	59
12	10	20	80-100°	5 min.	0.98	(contaminated with sulphonic acid)
13	10	20	80-100°	15 ,,	1.32	43 (very much contaminated with acid)

EXPERIMENTAL

Diazotisation of Sulphanilic Acid and the Preparation of Potassium p-*Nitrobenzene Sulphonate.*—Sulphanilic acid (34.6 g.) was gradually dissolved in water (170 c.c.) containing sodium carbonate (8.7 g.). The solution was warmed till sulphanilic acid dissolved. This was cooled to 15° (a small amount of the salt separated). To this was added a solution of sodium nitrite (12 g.) in water (35 c.c.). The resulting mixture was immediately poured into a solution of concentrated nitric acid (41 c.c.) and ice (200 g.). The diazo nitrate separated slowly. This was kept for about half an hour maintaining the temperature below 15°. To this suspension was added concentrated nitric acid (20 c.c.). In another beaker a suspension of cuprous oxide (5·6 g.) in water (300 c.c.) was taken. The suspension of the diazo salt was added gradually with stirring to the suspension of cuprous oxide when a brisk evolution of nitrogen took place. When the addition was over, the contents of the beaker were let stand overnight, filtered the next day and then warmed at 50°-60° for 15 minutes. Then the contents were exactly neutralised with a solution of potassium hydroxide (49 g.) in water (300 c.c.). The precipitated cupric hydroxide was filtered off and the filtrate evaporated to dryness. The solid thus obtained was dried at 100°-120° for 4 to 5 hours in a nickel basin ; yield of potassium *p*-nitrobenzene sulphonate, thus obtained, was 120 g.

Preparation of p-*Nitrobenzene Sulphonyl Chloride.*—Experiments (13) were conducted with various proportions of weights of phosphorus pentachloride and potassium *p*-nitrobenzene sulphonate. These are incorporated in Table I. The procedure followed is given below.

The potassium salt was taken in a round bottomed flask covered with a rubber stopper having a calcium chloride guard tube. Phosphorus pentachloride was added in small lots at room or slightly below room temperature (cooling, if the temperature goes up on the addition of PCl_5) and shaking the flask. After some time a pasty mass was obtained. This was heated on a water-bath for about an hour, cooled and the contents poured into a mixture of ice and water and ground well to decompose any excess of phosphorus pentachloride. The precipitated sulphonyl chloride was filtered, dried thoroughly first between the folds of filter paper and then in a vacuum desiccator. M. p. of the sulphonyl chloride is 78-79° and that of the amide prepared from this is 179°.

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FLUOBERYLLATES AND THEIR ANALOGY WITH THE SULPHATES. PART VIII. ADDITIVE COMPOUNDS OF AMMINOFLUOBERYLLATES WITH POTASSIUM AND AMMONIUM IODIDE

By Grihapati Mitra and Nirmalendu Nath Ray

The additive compounds of amminofluoberyllates of the type (M $6NH_3$) BeF_4, M'I were prepared, where M=Cu, Ni, Zn or Cd, and M'=NH_4 or K. As sulphates form similar compounds this furnishes further proof of the analogy between the sulphates and fluoberyllates.

Poma (*Atii R. Acad. Lincei*, 1909, *v*, **19**, 3) has shown that many of the amminosulphates of bivalent metals combine with potassium iodide, potassium bromide and potassium chloride molecules forming well defined molecular compounds. As complex amminofluoberyllates resemble the complex amminosulphates (Ray, *Z. anorg. Chem.*, 1939, **41**, 165) attempts have been made to isolate similar compounds. The present paper deals with the preparation and properties of the additive compounds of the complex amminofluoberyllates of nickel, zinc, copper and cadmium with potassium and ammonium iodide.

Experimental

Concentrated solution of the fluoberyllates was saturated with ammonia gas at or below 10°. The solution was quickly filtered and then treated with a saturated solution of potassium or ammonium iodide in liquor ammonia. The mixture was kept in a desiccator in an atmosphere of ammonia. The crystals that separated next day were filtered and dried over lime in an atmosphere of ammonia. The following compounds were obtained.

Table I

		M	I	Be.	NH_3.
1. (Cu $6NH_3$) BeF_4, KI	Found	10.89	43.34	1.57	17.56
	Calc.	10.91	43.55	1.55	17.54
2. (Cd $6NH_3$) BeF_4, KI	Found	17.92	40.20	1.42	16.21
	Calc.	17.79	40.18	1.43	16.18
3. (Zn $6NH_3$) BeF_4, KI	Found	11.06	43.46	1.53	17.60
	Calc.	11.18	43.42	1.54	17.48
4. (Cu $6NH_3$) BeF_4, NH_4I	Found	11.70	46.48	1.81	25.00
	Calc.	11.76	46.82	1.67	25.63
5. (Ni $6NH_3$) BeF_4, NH_4I	Found	10.84	47.38	1.83	25.53
	Calc.	10.95	47.37	1.69	25.81
6. (Zn $6NH_3$) BeF_4, NH_4I	Found	11.93	46.29	1.64	24.83
	Calc.	12.05	46.79	1.66	25.50
7. (Cd $6NH_3$) BeF_4, NH_4I	Found	19.01	43.45	1.30	23.05
	Calc.	19.06	43.04	1.53	23.46

The nickel compound is violet, the copper compounds are blue and the rest are white. While dry, the compounds are quite stable, but in presence of moisture they tend to lose ammonia and absorb water in its place. The compounds can be recrystallised from liquor ammonia. The magnetic susceptibility of the nickel compound was found to correspond with the value for Ni^{++} in other ordinary complexes. Attempts to isolate similar compounds with potassium chloride and bromide led to no successful results.

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VISCOSITY CHANGES DURING SOL-GEL TRANSFORMATION IN SOAP-NUJOL SYSTEM

By K. D. Deshpande

Viscosities of gel-forming systems of different concentrations of sodium oleate in Nujol have been measured at high temperatures during gelation. It is observed that at high temperatures (200°) the soap forms a molecular solution with little or no association, and cooling gives system like "isosols" and "isogels".

Viscosity shows the largest possible variation with even a small change in the colloid state, and hence, its determination has assumed a great importance in the investigation of colloidal systems. There is an added advantage that it can be measured accurately by comparatively simple methods. n the present investigation the viscosities of gel-forming systems of sodium oleate in Nujol have been measured during their continuous cooling from the temperature at which the solution is prepared to various temperatures.

Experimental

The falling sphere method was used for the determination of the viscosity. Details of the actual experimental technique followed and the observations regarding the fall of the spherical balls through gel systems are fully described by Prasad, Hattiangdi and Vishvanathan (*Proc. Ind. Acad. Sci.*, 1945, **21A**, 90).

The gel-forming solutions of sodium oleate in Nujol were prepared in the viscometer tube at 220° in the same manner as described by Prasad and co-workers (*loc. cit.*). The viscometer was then transferrred to an air thermostat maintained at 31° and was closed by a cork carrying a thermometer. When the temperature of the system reached 200°, the steel ball was dropped through the delivery tube and the time taken by it to travel the distance of 15 cm. was noted by means of a stop-watch. Such readings were taken at suitable temperature intervals till the last ball travelled the complete length.

B.D.H. sodium oleate and Nujol from Stanco, Inc. were used. Steel balls were manufactured by S.K.F. Ballbearing Co., their diameter was 0.15 ± 0.00025 cm. and specific gravity, 7.66.

The mean of a number of readings at the central portion of the tube has been given in each case in Table I in which t represents the time in seconds taken for the ball to fall through 15 cm., T_0, the temperature of the system in degree centigrade and η, the viscosity of the system in c.g.s. units.

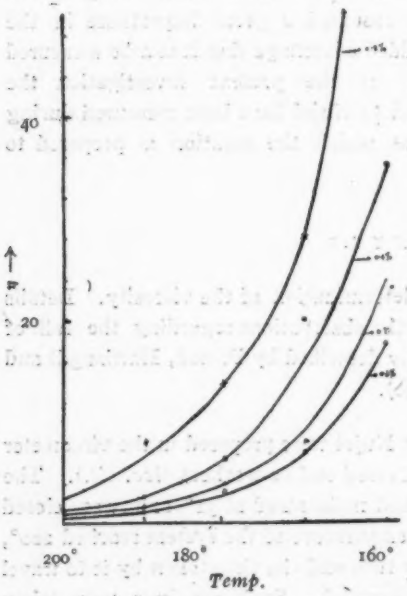
TABLE I

$T_\circ$.	c=0.2%.		c=0.3%.		c=0.4%.		c=0.8%.	
	t.	η.	t.	η.	t.	η.	t.	η.
200°	0.3″	0.621	0.4″	0.782	0.6″	1.174	1.2″	2.462
190°	0.6″	1.174	0.7″	1.476	1.3″	2.586	4.0″	7.930
180°	1.6″	3.130	2.0″	3.912	3.3″	6.317	6.7″	13.660
170°	3.6″	7.042	3.8″	7.966	9.4″	19.980	13.4″	28.080
160°	8.4″	17.664	11.0″	23.560	15.0″	34.930	29.6″	61.010
150°	13.2″	31.490						

DISCUSSION

The curves obtained by plotting the viscosities of the system of each concentration against temperature (that is during cooling) are shown in Fig. 1. All the curves are smooth; they rise at first slowly and then rapidly until they tend to become parallel to the viscosity axis as the temperature is systematically lowered. These observations are similar to those of Mardles (*Trans. Faraday Soc.*, 1923, **18**, 327) in the case of cellulose acetate gels in benzyl alcohol and of Prasad and co-workers (*loc. cit.*) in the case of soap gels in pinene.

FIG. 1

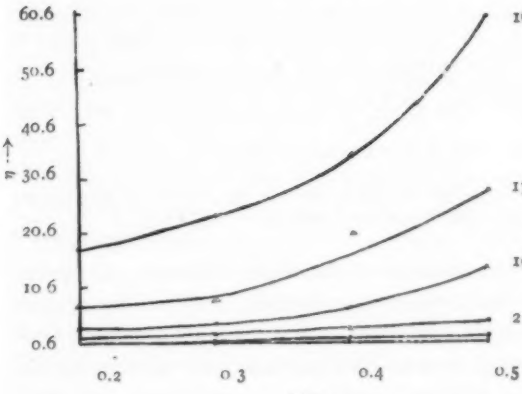


The applicability of Einstein's relation

$$\frac{\eta}{\eta_\circ} = 1 + K\theta$$

(where η is the viscosity of the solution, $\eta_\circ$, the viscosity of the solvent, θ, the proportion of the disperse phase to the entire volume and K. a constant) was tested by plotting for each temperature the values of η against c (assumed to be approximately proportional to θ). The curves shown in Fig. 2 bring out that the relation holds good only up to 200°. At 190° and below, the curve deviates from straight line character and the steepening of the curves progressively increases with lowering of the temperature. Since Einstein's relation is applicable to molecular solutions, it is inferred that the soap exists in the molecular state in Nujol at temperatures above 190° and goes over to the collodial state at about this temperature.

FIG. 2

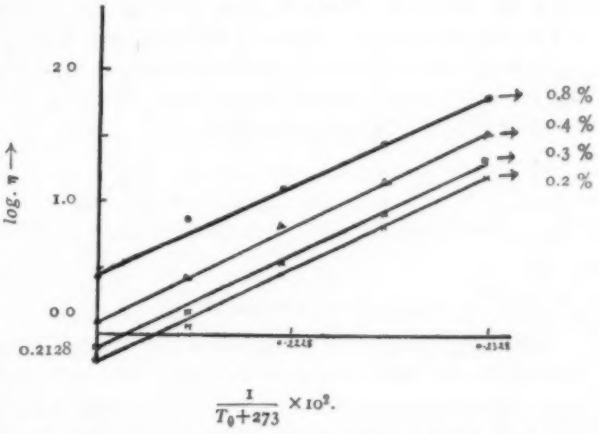


The graphs of logarithm of viscosity (log η) against the reciprocal of the absolute temperature ($1/T_a$) where $T_a = T + 273$, given in Fig. 3, are approximately straight lines, showing that a relation of the type

$$\eta = Ae^{E/RT_a}$$

(where A and E are constants) is followed. This relation is known ("Colloid Science" edited by Kruyt, Vol. II, p. 181) to express the variation of viscosity of "isosols" and "isogels" with absolute temperature, the "isosols" and "isogels" being colloidal systems formed from a mixture of small and large polymer molecules having the same chemical constitution. It may therefore be inferred that the system of sodium oleate in Nujol is akin to an "isogel". The suggests that the soap combines with the paraffins in Nujol and the resulting products polymerise to different degrees affording isosols first and then isogels on progressive cooling. The fact that soap and the paraffin in Nujol are long-chain aliphatic compounds goes to support this possibility.

FIG. 3



Thus, the variations in viscosity with temperature exhibited during the sol-gel transformation are in the beginning due to the passage of the molecular solution of the soap in Nujol to a colloidal solution at 190°. Subsequent changes are due to gel formation which results from (*i*) the gradual increase in the number and size of soap micelles, (*ii*) the solvation of the micelles with the dispersion medium which is a saturated solution of the soap in the solvent and (*iii*) the fusion of the solvated micelles into fibrils which form the gel structure enclosing the remaining liquid. The very rapid rise in viscosity during the later stages of cooling is probably due to the last reason.

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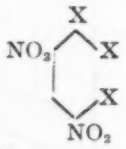
SOME TRIHALOGENATED NITROBENZENES AND THEIR DERIVATIVES. PART II

By Shiam Sunder Joshi and Veda Prakash Saxena

The preparation of forr trihalogenated benzenes, their nitration and the derivatives of the dinitro products with ammonia, diethylamine, aniline, piperidine, etc. are described.

The trihalobenzenes, viz., 1:2:3-tribromobenzene (Jackson and Gallivan, *J. Amer. Chem. Soc*, 1898, **20**, 1794), 1:3-dibromo-2-chlorobenzene (Hartley, *J. Chem. Soc.*, 1901, **79**, 1304), 1:2:3-trichlorobenzene (Cohen, *ibid.*, 1904, **85**, 1365) and 1:3-dichloro-2-bromobenzene (Hartley, *ibid.*, 1901, **79**, 1303) have all been prepared from sulphanilamide by first halogenating, then removing the sulphanilamido group and finally replacing the amino group in the aniline so obtained by a halogen atom (cf. Fuchs, *Monatsh*, 1915, **36**, 113). On nitration they all give the corresponding dinitro products, viz., 1:2:3-tribromo-4:6-dinitrobenzene (Jackson and Earle, *J. Amer. Chem. Soc.*, 1904, **26**, 50), 1:3-dibromo-2-chloro-4:6-dinitrobenzene, 1:2:3-trichloro-4:6-dinitrobenzene and 1:3-dichloro-2-bromo-4:6-dinitrobenzene (Sane and Joshi, this *Journal*, 1932, **9**, 61) which can be represented by the general formula



where X = a chlorine or a bromine atom.

In these dinitro compounds two of the halogen atoms (those in positions 1 and 3) have both the nitro groups in their *op*- positions. As such they are, as expected, reactive. They readily react with aniline, *o*- and *p*-toluidines, diethylamine, piperidine etc., and the halogen atoms in positions 1 and 3 are substituted by the corresponding groups. With ammonia, however, under similar experimental conditions, only one of the halogen atoms is replaced. The other, which resists the action of ammonia, can be subsequently replaced by a phenylamino group on heating with aniline.

Experimental

1:2:3-*Tribromobenzene*.—To a well cooled concentrated solution of sulphanilamide (10 g.) in acetic acid, bromine (19 g.), dissolved in acetic acid (12 c.c.), was added dropwise with continuous shaking. On keeping the product for a short time at room temperature pale yellow dibromosulphanilamide separated out (16 g.); it was washed with cold water, m.p. 234-38°.

For desulphonamidating, dibromosuphanilamide (10 g.) was heated with 70% sulphuric acid (50 c.c.) at 270°-280°, cooled and then treated with a current of steam; 2:6-dibromoaniline, which was volatile with steam, passed over (7 g.) and was crystallised from

alcohol, m.p. 87°. By subjecting it (10 g.) to Sandmeyer's reaction to replace the amino group by a bromine atom, it yielded 1:2:3-tribromobenzene (6 g.) on steam distillation. It was crystallised from alcohol, m.p. 87°.

1:3-*Dibromo-2-chlorobenzene* (6.5 g.) was similarly obtained from 2:6-dibromoaniline (10 g.) by replacing the amino group by a chlorine atom. It was crystallised from alcohol, m.p. 73°.

1:2:3-*Trichlorobenzene*.—Sulphanilamide (10 g.), dissolved in the least volume of dilute hydrochloric acid, was treated with hydrochloric acid (conc., 70-80 c.c.) whereby it was precipitated as hydrochloride. Potassium chlorate (5 g.) was added to the well cooled suspension in small amounts at a time with continuous shaking and cooling. The reaction mixture successively turned yellow, violet and bright red and 2:6-dichlorosulphanilamide began to separate from the thick mass in the form of rose-red crystals (6.5 g.). Purified by washing with water it melted at 203°-205°.

For removing the sulphanilamido group, 2:6-dichlorosulphanilamide (10 g.), suspended in 70% sulphuric acid (50 c.c.), was maintained at 270°-295° for 1½ hours. The dark coloured mixture was then cooled and poured in about 250 c.c. of water and the dark brown suspension distilled in steam, when 2:6-dichloroaniline (3.5 g.) passed over. It was crystallised from alcohol, m.p. 39°. From this compound (10 g.) 1:3-dichloro-2-bromobenzene (3 g.), m.p. 65° and 1:2:3-trichlorobenzene (5.5 g.), m.p. 53°, were obtained by replacing the amino group by the corresponding halogen atom.

1:2:3-*Trihalo*-4:6-*dinitrobenzenes*.—Nitration of these trihalobenzenes was effected by fuming nitric acid and concentrated sulphuric acid (Joshi and Gupta, this *Journal*, 1952, **29**, 193). All of them are pale yellowish white solids. Their melting points and analytical results are shown in Table I.

TABLE I

	Halobenzene used.	4:6-Dinitrobenzene obtained.	M.p.	Analysis. Found.	Calc.
(*i*)	1:3-Dibromo-2-chloro-	1:3-Bromo-2-chloro-	135°	BrCl, 54%	54.1 %.
(*ii*)	1:2:3-Tribromo-	1:2:3-Tribromo-	153°	Br, 59.7	59 24.
(*iii*)	1:2:3-Trichloro-	1:2:3-Trichloro-	98°	Cl, 39.4	39.15.
(*iv*)	1:3-Dichloro-2-bromo-	1:3-Dichloro-2-bromo-	106°	ClBr, 47.9	47.74

Some derivatives of these trihalodinitrobenzenes (which have two reactive halogen atoms in positions 1 and 3) have been prepared by boiling their alcoholic solutions with ammonia, aniline, *o*- and *p*-toluidines etc., for about an hour (Joshi and Gupta, *loc. cit.*). With ammonia, only one of the reactive halogen atoms reacts forming a different aniline in each case. The other reactive halogen atom can be subsequently replaced when heated with aniline. With other reactants both reactive halogen atoms are substituted. Identical products are obtained from 1:3-dibromo-2-chloro-4:6-dinitrobenzene(*i*) and 1:2:3-trichloro-4:6-dinitrobenzene(*iii*) and from 1:2:3-tribromo-4:6-dinitrobenzene(*ii*) and 1:3-dichloro-2-bromo-4:6-dinitrobenzene (*iv*). Colour and melting points of these derivatives are shown in Tables II and III.

TABLE II

Derivatives of 1:3-*dibromo*-2-*chloro*-4:6-*dinitrobenzene* (*i*) *or of* 1:2:3-*trichloro*-4:6-*dinitrobenzene* (*iii*).

Reactant.	Derivative.	Colour.	M.p.
Aniline	2 Chloro-1 :3-dianilino-X	Bright orange	187°-88°
o-Toluidine	2-Chloro-1 :3-di-*o*-toluidino-X	Dark brick red	173°
p-Toluidine	2-Chloro-1 :3-di-*p*-touidino-X	Dull orange-red	217°-19°
Diethylamine	2-Chloro-1 :3-di-diethylamino-X	Light lustrous orange	81°
Piperidine	2-Chloro-1 : 3-dipiperidino-X	Yellow	191°
Ammonia with (*i*)	2-Chloro-3-bromo-Y	Bright yellow	207°-208°
Ammonia with (*ii*)	2 : 3-Dichloro-Y	Bright yellow	188-89°
Ammonia and aniline	2-Chloro-1-phenylamino-Y	Dull orange	195 97°

X=4 : 6-dinitrobenzene.
Y=4 : 6-dinitroaniline.

TABLE III

Derivatives of 1:2 :3-*tribromo*-4:6-*dinitrobenzene* (*ii*) *and* 1:3-*dichloro*-2-*bromo*-4:6-*dinitrobenzene* (*iv*).

Reactant.	Derivative.	Colour.	M.p.
Aniline	2-Bromo-1 :3-dianilino-X	Shining orange	199°
o-Toluidine	2-Bromo-1 :3-di-*o*-toluidino-X	Dull brick-red	167°
p-Toluidine	2-Bromo-1 :3-di-*p*-toluidino-X	Orange-red	175°
Diethylamine	2-Bromo-1 :3-di-diethylamino-X	Light orange	90-91°
Piperidine	2-Bromo-1 :3-dipiperidino-X	Dull yellow	176°
Ammonia with (*ii*)	2 :3-Dibromo-Y	Yellow	219°
Ammonia with (*iv*)	2-Bromo-3-chloro-Y	Yellow	204°
Ammonia and aniline	2-Bromo-3-phenylamino-Y	Dull orange	205-206°

X and Y have the same significance as in Table II.

Identity of the derivatives obtained from each pair of the trihalodinitrobenzenes was established by determining mixed melting points and by analysis.

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STUDIES ON RICE HUSK, BETELNUT HUSK, AND BAMBOO LIGNINS. PART I. ISOLATION BY DIFFERENT METHODS

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The Klason and Willstätar lignins obtained from rice husk were found to retain considerable proportions of ash and cellulosic materials. Similar impurities were found in lesser proportions in products from betelnut husk, and least in bamboo lignins The percentage of impurities were determined in all cases. The true Klason lignin (after correction) was found to be 24.10,27.56 and 27.45% respectively for rice husk, betelnut husk and bamboo. The corresponding values for Willstätar lignin were 19.50, 22.93 and 24.22 respectively. Acetic acid lignin values were much lower in all cases.

Methoxyl values were determined on the crude samples, and threfrom computed for the actual lignin content. The values are only slightly different for the different raw materials (11.13% to 15.81%), and practically independent of the method of isolation.

The structure of the lignin molecule is not quite fully understood. There arises confusion even with the building components. Thus, while vanillin is the principal product from alkaline treatment of coniferous wood, both vanillin and syringaldehyde are obtained from similar treatments of hard wood (Hawkins, Wright and Hibbert, *J. Amer. Chem. Soc.*, 1937, **59**, 2447). Even when dealing with similar type of sources, the elementary composition or group concentration appears to vary. The methoxyl content has been found to vary from as low as 9.90% (Freedman and MacCully, *Paper Trade J.*, 1938, **107**, 28) to as high as 21.0% (Sherrard and Harris, *Ind. Eng. Chem.*, 1932, **24**, 103), depending on the source. The variation can be somewhat accounted for by recognising that except what is obtained by the method of Braun (*J. Amer. Chem. Soc.*, 1939, **61**, 2120), a lignin preparation is isolated which is no longer identical with the native lignin (proto-lignin). Obviously the course of change is not also the same in all methods. Acid lignins (those isolated by dissolving out the carbohydrates with strong acids) change both physically and chemically. Other methods give us lignins in the form of their derivatives, which are finally decomposed. So, in the present state of our knowledge the undefined term 'lignin' does not signify any definite meaning. Lignin should better be used as a collective term for a group of highly polymerised compounds of very similar chemical properties. And in order to refer to any particular sample of lignin, it is necessary to specify the source and method of isolation.

The present investigation deals with the isolation of lignin with special stress on the yield, purity and characteristics such as methoxyl content Rice husk, betelnut husk and bamboo were chosen as the raw materials because of their ready availability and cheapness. The case of rice husk is particularly interesting as it has been reported (Chowdhury and co-workers, *J. Indian. Chem. Soc., Ind. & News Ed.*, 1947, **10**, 40) to contain an unusually high percentage of lignin. A value for the Willstätar bamboo

lignin is also available (Sarkar, this *Journal*, 1934, **11**, 691). No information is available for the betelnut husk. In the present investigation, however, a comparative study of the products obtained from these sources by a number of methods has been undertaken. Klason and Willsttätar methods were employed, because commercially available isolated lignins (through saccharification) are obtained by the use of similar reagents. A method for alkali lignin was chosen (acetic acid method) so that it would give the least changed product.

In subsequent communications will be reported results on nitration and nitric acid degradation of these lignins.

Experimental

Prior to treatment, each of the starting materials was washed with water to free it from dust etc., air-dried and ground to 60 mesh powder, washed again with distilled water, air-dried, and finally extracted with 1:1 alcohol-benzene mixture, again air-dried, and finally heated to 80° for 15 minutes (to drive off all the solvents). This was used as the stock sample. For details of the first two methods of isolation (Klason and Willsttätar methods) reference may be made to the original work, or any standard text book. For the acetic acid lignin a procedure as laid down by Braun and Buchanon (*J. Amer. Chem. Soc.*, 1945, **67**, 645) was followed. The yields in the various methods with the different raw materials are shown in Table I. In the acetic acid method, proportions obtained in the different fractions are also given.

Table I

Method employed	Yield of crude lignin (% by wt.).		
	Rice husk.	Betelnut husk.	Bamboo.
Klason	40.02	31.09	29.00
Willsttätar	36.20	27.00	26.05
Acetic acid:			
1st fraction 8.00	10.10	11.63	
2nd fraction 2.92	3.23	4.60	
3rd fraction 1.12	2.04	2.50	
Total 12.04	15.37	18.73	

All preparations were light brown in colour. The depth of the colour was in general greater for the Klason lignins. The acetic acid lingins gave dark solutions in dioxane (other lignins are insoluble). Evaporation of the dioxane left a dark resinous mass. Purification of acetic acid lignins from this solution often offered great difficulties, which were finally solved by adopting the following procedure.

A 10% solution of acetic acid lignin in anhydrous dioxane was dropped through a very fine jet in a dropping funnel into a considerably large volume of ether taken in a conical flask (vigorously shaken to enhance dispersion). This helped all the dioxane to dissolve in ether, thereby leaving a light coloured lignin deposit (the colour was much lighter than those obtained by any of the other two methods). The mass was decanted carefully, washed thoroughly with petroleum ether and dried at 60° when

a straw-coloured product was obtained. During the purification process, when the lignin was finally dispersed in ether and allowed to stand, particles were observed to move to and fro and tended to form bigger particles, probably indicating that very fine particles of the colloidal order were initially formed through dispersion.

It has been suggested by Braun (*Tech. Assoc. Paper Pulp Ind.*, 1949, **32**, 157) that proto-lignin is colorless. The colour of the isolated lignins may thus be due either to polymerisation already present in the plant material (Freudenberg, *Ann. Rev. Biochem.*, 1939, **8**, 88) or due to polymerisation taking place during the process of isolation. In the present case the three raw materials before extraction with benzene-alcohol were differently coloured. The colour in all cases could be due partly to the resinous material (removed by the alcohol-benzene), and partly due to iron present in them, which was actually detected in the ash. No final conclusions can thus be made about the extent of polymerisation of these crude lignins without a direct measurement of the degree of polymerisation.

Analysis of the Crude Lignins and Correction for Ash and Cellulose in them

The results obtained above by the different methods were very unusual. In the first place, the acid lignins gave much higher yields than the acetic acid lignins. A low value for acetic acid lignin, of course, is quite easily understood in recognition of the reagent employed, but the difference is too large to be explained on this basis alone. The starting materials were characterised by a high percentage of ash (rice husk 12.7%, betelnut husk, 5.47 and bamboo, 3.85%). It was felt that in the presence of strong acids employed in the first two methods, some of the inorganic constituents might have been left in the lignin. This was actually found to be so. Results of determination of ash on all crude lignin samples are given in Table II. As expected, acetic acid lignins did not give any measurable proportions of ash content.

It was further observed that while acetic acid lignins were in all cases easily soluble in dilute caustic soda solution, the other samples were only partly soluble in 17.5% NaOH even on boiling. The Klason and Willstätar crude lignins were thus treated with 10% NaOH under pressure, when some residues were obtained in all cases. This obviously were the cellulosic materials that evaded dissolution by the reagents under conditions of the experiments. The cellulosic materials in the crude lignins were indirectly determined by the hypochlorite method. From this value and that of the ash content, the actual lignin content of the respective samples was calculated from the equation :

$$L = Y - \frac{(c+a)\,Y}{100}$$

where L = actual lignin content of the raw material (% by wt.), Y = yield of crude lignin (% by wt. of raw material), c = cellulose in crude lignin (% by wt.) and a = ash in crude lignin (% by wt.).

TABLE II

Corrected yield of lignin from crude lignin values.

Raw material.	Method of isolation.	Yield of crude lignin (Y).	Cellulose in crude lignin (c).	Ash in crude lignin (a).	Actual lignin content (L).
Rice husk	Klason	40.02	12.05	27.71	24.10
,,	Willsttatar	36.20	15.82	30.31	19 5c
Betelnut husk	Kl	31.09	2.19	9 16	27.56
,,	W	27.00	5.50	9.56	22.93
Bamboo	Kl	29.00	1.19	4.14	27.45
,,	W	26.05	3.14	3.89	24 22

The corrected values for the lignins from various sources were quite reasonable. The higher values for the crude lignin were due to ash and cellulose present in them. These impurities were in the decreasing order from rice husk, through betelnut husk to bamboo. The presence of cellulose in the crude lignins might be indicative of the relative strengths (tenacity) of the lignin-cellulose linkage in the different raw materials : or may be, the ash contents have some directive influence on the dissolution of cellulose by the acidic reagents. It will be further observed that the Willsttätar lignin yields were in all cases less than those obtained by the Klason method. Similar observations were also made by Phillips (*J. Assoc. Offic. Agrl. Chem.*, 1938, **21**, 145). The Willsttätar method thus cannot be reliably employed for purposes of characterising the lignin content of a particular sample of cellulosic material. The acetic acid lignin yields were also unexpectedly low.

Methoxyl Content of the various Lignin Samples

The methoxyl content was determined on the crude lignin samples by the standard Zeisel method, and the values are recorded in Table III.

TABLE III

Method of isolation	Rice husk	Betelnut husk.	Bamboo.
Klason	6.70%	12.98%	14.97%
Willsttätar	6.01	12.49	14.10
Acetic acid :			
1st fraction	10.17	11.20	12.97
2nd fraction	9.87	11.17	12.93
3rd fraction	9 80	11 07	12.61
Value on purified product	10 20	11.50	13 20
Corrected(acetic acid lignin)value	12.20	13.50	15 20

The methoxyl values for the different fractions of the acetic acid lignins were found to agree fairly well, showing that this property was not particularly affected by the duration of digestion. The purified lignin values shown in the table are those obtained on the mixture of all the fractions after being purified by dispersion in ether from a dioxane

solution. The methoxyl content of the Klason and Willsttätar lignins were found to be abnormally low, due to the ash and cellulose contaminations. The values were gradually higher with betelnut husk and bamboo respectively. The corrected values (calculated on the basis of these impurities) are given in Table IV. It was observed (Braun and Buchanon, *loc. cit.*) that the methoxyl values were lower, due to partial acetylation, for the acetic acid lignins obtained from spruce. A correction of +2.0% was thus applied to the values of the acetic acid lignins.

TABLE IV

Method of isolation.	Rice husk	Betelnut husk	Bamboo.
Klason	11.13%	14.64%	15.81%
Willsttätar	11.16	14.71	15.17
Acetic acid(+2.0%)	12.20	13.50	15.20

It will be clear that the methods of isolation have no particular effect on the methoxyl content of any particular sample. The actual values for the several raw materials studied vary to some extent. Rice husk has a little low value (average about 11.50%), betelnut husk giving a lignin with a methoxyl content of 14.28% (average), while the values for bamboo would be 15.39%.

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STUDIES IN CLAISEN REARRANGEMENT. PART II. REARRANGEMENT OF ALLYL-*p*-*tert*.-AMYLPHENYL ETHER

By A. B. Sen and R. P. Rastogi

Allyl-*p*-*tert*.-amylphenyl ether has been thermally rearranged to *o*-allyl-*p*-*tert*.-amylphenol and several derivatives of the phenol have been prepared.

In continuation of our studies on the rearrangement of *p*-substituted alkylphenyl-allyl ethers (this *Journal*, 1953, **30**, 355), we have now subjected allyl-*p*-*tert*. amylphenyl ether to thermal treatment and prepared a number of important derivatives of the rearranged product.

The allylphenyl ether rearranged smoothly on heating at 210°-220°, yielding 89% of *o*-allyl-*p*-*tert*.-amylphenol; the separation of the phenol from the reaction mixture was effected by using very dilute alkali and allowing some time for separation. The allylphenol was characterised through its carbomethoxy ether derivative. Its 3:5-dinitrobenzoate was obtained as a viscid yellow mass which could not be crystallised.

Oxidation of allylphenol with $KMnO_4$ in acetone solution gave coloured products, as in the case of allyl-*p*-*tert*.-butylphenol (*loc. cit.*)., and it was therefore subjected to oxidation after conversion into its methyl ether. The pale, viscid acidic component, thus obtained, could not be crystallised but was identified through its crystalline derivative, 2-methoxy-5-*tert*.-amylphenylacetanilide. The allylphenol was catalytically reduced to the propylphenol in 85% yield. Isomerisation of the allylphenol to the propenylphenol was effected by heating it with caustic soda, but, as in the case of the allyl-*p*-*tert*.-butylphenol (*loc.cit.*), a higher distilling fraction was also obtained which appeared to be, on the basis of M. W. estimation, a mixture of high polymers.

2-Methyl-2:3-dihydro-*p*-*tert*.-amylbenzofuran was obtained in 68% yield as a result of ring-closure in the allylphenol molecule by heating with pyridine hydrochloride. But unlike the case of *o*-*allyl*-*p*-*tert*.-butylphenol (*loc. cit.*), this compound could not be compared by another method, as the mercuration of the allylphenol yielded a petrol ether-soluble, semi-solid product which failed to crystallise from any solvent. Its purification by distillation in high vacuum gave an oily liquid at the bath temperature of 185°-190°/10^{-4} mm. along with some mercury globules. This liquid contained less than 1% of Hg, showing that decomposition occurred during the process, and further experiments with mercurated benzofuran were therefore discontinued.

Experimental

p-tert.-*Amylallylphenyl Ether.*—*p*-*tert*.-Amylphenol (60 g.), allyl bromide (60 g.), anhydrous potassium carbonate (72 g.) and dry acetone (150 c.c.) were refluxed on a water-bath with stirring for 8 hours. After removal of the acetone, the reaction mixture was extracted with ether. The ethereal layer was successively washed with dilute caustic

soda solution and water, and dried over anhydrous sodium sulphate. The oily residue left after removal of the ether was distilled under reduced pressure, b.p. 142-43°/7 mm., yield 66 g., n_D^{32}, 1.508. (Found: C, 82.8; H, 10.0. $C_{14}H_{20}O$ requires C, 82.3; H, 9.7 per cent).

o-*Allyl*-p-tert.-*amylphenol*.—The allyl ether (40 g.) was heated at 210°-220° for 2 hours in an atmosphere of carbon dioxide. The reaction mixture was taken up in ether and extracted repeatedly with 2% caustic soda. The combined alkali solution was acidified and worked up in the usual manner. The amylphenol distilled at 136-37°/4 mm., yield 34 g., n_D^{32}, 1.5223. It is soluble in dilute alkali and gives an olive-green coloration with ferric chloride. (Found: C, 82.5; H, 9.7. $C_{11}H_{20}O$ requires C, 82.3; H, 9.7 per cent).

o-*Allyl*-p-tert.-*amylphenylcarbomethxy Ether*.—A solution of the allylphenol (0.5 g.), 33% caustic potash (2 c.c.) and 50% monochloroacetic acid solution (1.4 c.c.) were heated on a water-bath for 2 hours and then worked up according to the procedure outlined earlier. The final residue gave the crystalline derivative from dilute alcohol, m.p. 71°, yield 25 mg. (Found: C, 73.5; H, 8.3. $C_{16}H_{22}O_3$ requires C, 73.2; H, 8.4 per cent).

o-*Propyl*-p-tert.-*amylphenol*.—A methanolic solution of the allylphenol (2 g.) was catalytically reduced with platinum black in hydrogen atmosphere; 262 c.c. of hydrogen were absorbed at 26°/75.4 cm. The residual oil was fractionated under reduced pressure, b.p. 113-14°/1 mm., yield 1.7 g., $n_D^{32.5}$, 1.507. (Found: C, 81.5; H, 10.8. $C_{14}H_{22}O$ requires C, 81.5; H, 10.6 per cent).

o-*Allyl*-p-tert.-*amylphenylmethyl Ether*.—The allylphenol (5 g.) on reaction with dimethyl sulphate (9 c.c.) in caustic soda solution (20%) gave the methyl ether distilling at 99°-101°/1 mm., yield 4.2 g., n_D^{32}, 1.506. (Found: C, 82.4; H, 10.0. $C_{15}H_{22}O$ requires C, 82.5; H, 10.0 per cent).

Oxidation of o-*Allyl*-p-tert.-*amylphenylmethyl Ether*.—A solution of the methyl ether (1.8 g.) in acetone was oxidised with potassium permanganate (2.3 g.) according to the conditions described earlier.

The acidic component could not be crystallised through any solvent and was converted into the acid chloride by refluxing with thionyl chloride. The residue, obtained after removal of the excess of thionyl chloride, was cooled and treated with aniline. The reaction mixture was extracted with ether and the ethereal solution washed with dilute hydrochloric acid and water, then desiccated and freed of the solvent. The residue was subjected to distillation, when the anilide distilled over at bath temperature of 210°-215°/10^{-4} mm. It crystallised in the distillation bulb and was freed of the matrix by a little cold alcohol. It was obtained as colorless needles, m.p. 128°, yield 95 mg. (Found: N, 4.75. $C_{20}H_{25}O_2N$ requires N, 4.5 per cent).

Isomerisation of o-*Allyl*-p-tert.-*amylphenol to* o-*Propenyl*-p-tert.-*amylphenol*.—The allylphenol (5 g.), caustic potash pellets (10 g.) and water (5 c.c.) were heated together at 175°-180° for 1 hour. The reaction product was worked up in the usual manner and the viscid residue was fractionated twice under reduced pressure. The following fractions were collected.

(*i*) 114°-116°/0.5 mm. (0.9 g.). It is mainly the unchanged allylphenol.

(*ii*) 118°-120°/0.5 mm. (2.8 g.). It is the propenyl derivative, $n_D^{32} = 1.5355$. (Found: C, 81.8; H, 9 4. $C_{14}H_{20}O$ requires C, 82.3; H, 9.7 per cent).

(*iii*) 140°-200°/0.5 mm. (1.2 g.). it is a semi-solid, sticky mass. M.W. (Rast), 357.

2-Methyl-2:3-dihydro-p-tert.-*amylbenzofuran*.—The allylphenol (5 g.) and pyridine (1 g.) were heated together at 220° for 2 hours. The reaction mixture was poured in dilute alkali and extracted with ether. The residual oil from the neutral layer was distilled under reduced pressure and the following fractions were collected.

(*i*) 106°-110°/1 mm. (3.4 g.), $n_D^{32} = 1.513$. It gives a deep violet dye on treatment with isatin in concentrated sulphuric acid. (Found: C, 82.1; H, 9.7. $C_{14}H_{20}O$ requires C, 82.3; H, 9.7 per cent).

(*ii*) 150°-210°/1 mm. (1.3 g.). It is a pale semi-solid which does not absorb bromine in CCl_4 solution.

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AN INVESTIGATION INTO THE VISCOUS PROPERTIES OF GUM JEOL. (*ODINA WODIER*, ROXB.) *

By N. K. Maitra

Viscous properties of the purified gum and gum-acid have been studied with reference to the effect of heat and *p*H Pure gum exhibits higher viscosity than the gum-acid.

Gum Jeol (*Odina Wodier*, Roxb. and *Lannea grandis*, Engl.) is an indigenous gum of India and found in abundance all over Bengal, Assam and Burma. During recent years Mukherjee and co-workers (this *Journal*, 1948, **25**, 59, 63, 113) have studied some of the physico-chemical properties of the gum. But very little work has been done on the viscous properties of the gum or its other products. In the present investigation, an attempt has been made to study some of the viscous properties of the gum.

Experimental

Measurements of viscosities in the present investigation were carried out in a rotary viscometer of the Couette type, details of which have been published elsewhere (Mukherjee and Sen Gupta, *Indian J. Phys.*, 1942, **16**, 66).

Before any experiment was carried out, it was thought necessary to calibrate the instrument and to check the reproducibility of results obtained by it.

Experiments were carried out with 60% glycerol and 20%, 40% and 60% canesugar solutions and these calibration experiments comprised a considerable amount of work, not mentioned here for economy of space ; only the results have been shown in Table I. It was observed during these preliminary experiments that for reliable measurements the maximum rate of shear should be about 120 cm./sec./cm. and the minimum about 20 cm./sec./cm. In the present experiments therefore the rate of shear was strictly between these limits.

Table I

With 60% glycerol.

Trial No	I.	II	III.	IV.	V.	VI.
Temperature	23.9°	23.9°	22.7°	23.4°	23.3°	23.0°
Viscosity coefficient (experimental)	9.227	9.366	9.83	9.472	9.465	9.673
Viscosity coefficient (standard data)	9.240	9.240	9.74	9.45	9.49	9.61
% Error	−0.25	1.4	0.9	0.2	−0.32	0.65

With 20% canesugar.

	I.	II.	III.	IV.
Temperature	25.5°	24.6°	25.4°	24.5°
Viscosity coefficient (experimental)	1.696	1.718	1.684	1.741
Viscosity coefficient (standard data)	1.69	1.728	1.694	1.734
% Error	0.35	−0.61	−0.63	− 0.4

With 40% canesugar.

Temperature	24.5°	24.5°	22.8°	23.1°
Viscosity coefficient (experimental)	5.223	5.257	5.58	5.557
Viscosity coefficient (standard data)	5.28	5.28	5.62	5.56
% Error	−1.08	−0.46	-0.8	0.2

* This piece of work was carried out in 1942.

TABLE I (contd.)

With 60% canesugar.

	I.	II.	III.	IV.
Temperature	21.7°	22.0°	21.4°	21.4°
Viscosity coefficient (experimental)	52.60	51.15	52.76	52.12
Viscosity coefficient (standard data)	52.00	51.00	52.62	52.62
% Error	1.15	0.3	0.28	−0.95

It is thus clear that the viscosity coefficients obtained with the help of this instrument agree quite well with standard data within ±1% (International Critical Tables, 1029, Vol. V).

Purification of the Gum.—The raw gum was suspended in distilled water and kept for three days. The gum swelled and it was sieved through a piece of cloth thereby removing the fibrous materials The gum was then precipitated with rectified spirit as a white substance in the colloidal state. It was then coagulated by the addition of a small quantity of 5% NaCl solution. After allowing it to stand for a few hours the supernatant liquid was decanted off and the precipitated gum dissolved in minimum quantity of distilled water. It was reprecipitated with rectified spirit and the processes of solution and precipitation were repeated four times. Finally, the solution of the gum was centrifuged to get rid of the suspended impurities.

Preparation of the Gum-acid.—The method used for the preparation of the gum-acid was developed in this laboratory. The purified gum was treated with $N/10$-HCl and kept overnight. It was then dialysed through parchment paper and finally electro-dialysed till free from Cl^-, Ca^{++} and Mg^{++} ions.

In the present investigation the following features have been examined.

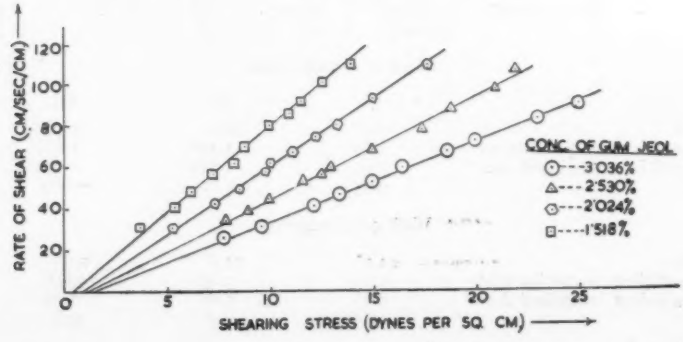
(*i*) Viscous properties of the purified gum at different concentrations.

(*ii*) Viscosity of the gum-acid at different concentrations.

(*iii*) Effect of p_H on the viscous properties of the above acid.

(*i*). *Viscosity of the Purified Gum.*—Results of viscosity measurements by the rotary viscometer have been graphically shown in Fig. 1. Concentrations of the solutions were determined by evaporating a known volume of the solution in a platinum crucible over the water-bath till the weight was constant.

FIG. 1

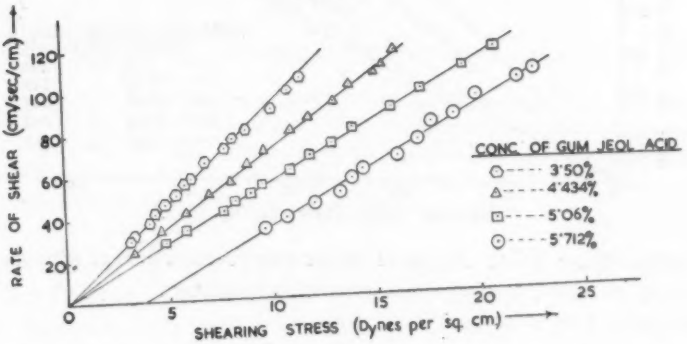


All the solutions show yield values which have been observed to increase with concentration, as evident from the graph.

(ii). Viscosity of the Gum-acid.—Viscosities at different concentrations of the gum-acid are shown in Fig. 2.

Solutions exhibit yield values beyond a concentration of 5.06%. For the same concentration, the acid is much less viscous than the gum and the yield-value also appears at a much higher concentration.

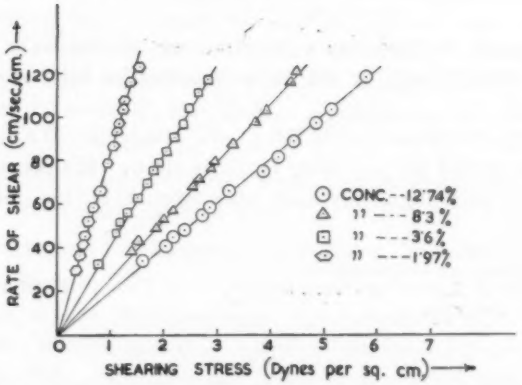
FIG. 2



Effect of Heating on the Viscosity of the Gum-acid.—A dilute solution of the gum-acid was concentrated over the water-bath to different concentrations, and viscosities measured. Some of the results are shown in Fig. 3.

Heat treatment reduces the viscosity very much. Whether it has anything to do with the disappearance of some probable gel structure is, however, not clear.

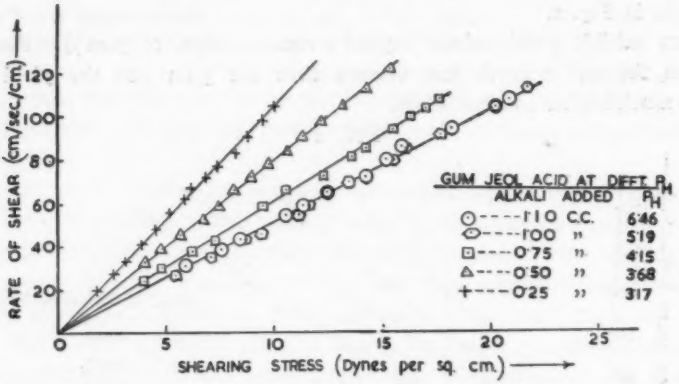
FIG. 3



(iii). Effect of p_H on the Viscous Properties of Gum-acid.—The original gum-acid solution (40 c.c.) of known concentration was taken in several bottles. Different amounts of 1.012 (*N*) NaOH solution were added to each of them and necessary amount of water added to make up the volume to 50 c.c. The final concentration of the gum-acid was 2.8% in all cases.

p_H was measured by means of hydrogen electrode. Some of the results of viscosity measurement are shown in Fig. 4.

FIG. 4



These experiments point out some interesting features in that with the increase of p_H the viscosity increases, reaches a maximum corresponding to a p_H of 6.46, and then goes on decreasing with further increase of p_H.

CONCLUSION

It has been observed that the pure gum has always a higher viscosity than the gum-acid. Yield-values appear at a much lower concentration for the gum than the gum-acid. The gum-acid cannot stand a high temperature (100°), its structure is in all probability broken down to some simpler form having much lower viscosity. The addition of alkalies has a remarkable effect on the viscosity of the gum-acid (Fig. 4).

While the gum-acid at moderate concentrations behaves as a Newtonian liquid, the gum, on the other hand, at the same concentration behaves as a non-Newtonian liquid.

The author's best thanks are due to Dr. J. N. Mukherjee, D.Sc., F.N.I., for keen interest in the work and for the laboratory facilities given. His thanks are also due to Dr. M. K. Indra for rendering him considerable amount of help during the course of the investigation.

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STUDIES ON *p*-AMINOSALICYLIC ACID DERIVATIVES (DYES). PART I

By SIBA NARAYAN MAHAPATRA AND S. S. GUHA SIRCAR

A number of azo dyes of *p*-aminosalicylic acid (P A S) have been prepared The antibacterial action of these compounds has been studied against *E.Coli*, *Staphylococcus aureus* and *Mycobacterium phlei* in Kirchner's synthetic medium. Measurement of toxicities of the mercurated azo dyes obtained from P A S. by means of perfusion experiments on the isolated frog's heart shows that the mercurated azo dyes are not very toxic even at a concentration of 1 :1,000.

A very large number of biologically active natural and synthetic compounds of various groups, e.g., vitamines, antibiotics, glucocides, coumarin and anthraquinone derivatives and vegetable toxic principles affecting insects or mammals, are known to contain multiple functional groups like OH, CHO, CO, COOH, CH_2OH, lactone and primary, secondary or tertiary amine. *p*-Aminosalicylic acid, which is highly active against *Mycobacterium tuberculosis*, also exemplifies this apparently general rule.

In the present paper a study has been made of the effect of introducing another group like the phenylazo or mercurated phenylazo group into this molecule in the expectation of attaining higher activity against the more common pathogenic bacteria, which are generally known to be insensitive to P A S. This hope has, to a certain extent, been realised and some of the mercurated azo dyes have proved highly active in dilutions of the order of 1/400,000 and 1/500,000 against *Staphylococcus aureus*. The order of activities of some of the known organomercurials against the same organism are given below.

Phenylmercuri chloride, 1/192,000; Merthiolate, 1/120,000; Metaphen, 1/140,000; Mercurochrome, 1/160 ; mercuric chloride, 1/1,000,

These data are taken from "Pharmacological Basis of Therapeutics" by Goodman and Gilman, New York, 1948, p. 856.

The only reference to azo dyes involving P A S are found in the work of Bhate, Panse and Venkataraman, who diazotised P A S and coupled it with β-naphthol (*Proc. Ind. Acad. Sci.*, 1949, **29A**, 199), and also a few others by the same authors (*ibid.*, 1950, **32A**, 360), who diazotised sulphanilamide and aniline and coupled them with P A S under neutral and alkaline conditions.

The compounds described in this paper were prepared by coupling some diazotised aromatic primary amines with P A S in alkaline medium (Table I), by

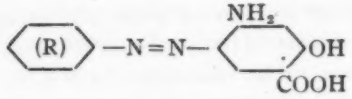
coupling the diazotised bases with the methylol derivative of P A S (Table II), and by coupling some diazotised mercurated bases with P A S in acetic acid medium (Table IV).

The toxicities of some of the mercurated azo dyes have been studied by perfusing their solutions at different concentrations through the isolated frog's heart, by standard Kymographic technique. The details and results of these experiments are being communicated elsewhere. It may be stated here, however, that the compounds were not found to show serious toxicities in concentartions lower than 1/1,000. This indicates that they may prove harmless to higher animals in therapeutic doses.

EXPERIMENTAL

The simple azo dyes were prepared by diazotising the aromatic primary bases to which 2½ moles of *N*-HCl were added, followed by one mole of $NaNO_2$, in 10% solution, dropwise below 5°, till the starch-iodide indicator paper just turned blue. The diazotised solution was then added dropwise to P A S, dissolved in 2½ moles of *N*-NaOH solution at that temperature. The reaction mixture was stirred for half an hour to ensure complete coupling. The final mixture was acidified with 4*N* acetic acid in order to liberate the dye completely, while the stirring was continued. The precipitate was filtered at the pump, washed with water and finally crystallised from rectified spirit and dried in the steam-oven.

Most of the dyes were found to be crystalline possessing brown, orange or red colour. They were soluble in alkalies, ammonia and also in ethylene glycol. They have the following general structure



where (R) is some substituent lika -Cl, $-NO_2$, $-CH_3$ etc., which occupied either the *ortho*, *meta* or *para* position of the benzene ring. The estimation of nitrogen in the azo compounds was done by first reducing them with alcoholic alkaline $Na_2S_2O_4$ solution. The concentrated mixture was then treated with concentrated H_2SO_4 and the digestion completed as in Kjeldahl's method in the usual way.

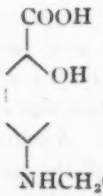
The antibacterial activities of the azo dyes were tesed against *E. Coli*, *Staphylococcus aureus* and *Mycobacterium phlei* in Kirchner's synthetic medium using the Rideal-Walker serial dilution method since ordinary broth media,p repared from 'lemco', contained PABA which acts as an antagonist to P A S and its derivatives. The results are tabulated as follows.

The melting points and the nitrogen estimation data of the azo dyes obtained by coupling the diazotised solutions of the following bases in alkaline P A S solution are tabulated below. The compounds were active up to a dilution of 1:1,000 towards *E. Coli* and *M. phlei*. The activity towards *Staph.aureus* is noted against each compound.

TABLE I

Bases diazotised.	M.p. of azo comp.	% Nitrogen. Calc.	Found.	M.E.D. *Staph. aureus.*
Aniline	199°	16.4	16.34	1 :1,000
o-Toluidine	195°	15.5	16.32	1 :1,000
m-Toluidine	197°	15.5	15 86	1 :1,000
p-Toluidine	201°	15.5	14.80	1 :1,000
o-Chloroaniline	210°	14.4	13.96	1 :3,000
m- ,,	202°	14.4	14.03	1 :2,000
p- ,,	208°	14.4	14.05	1 :2,000
o-Nitroaniline	202°	18.55	17.98	1 :3,000
m- ,,	210°	18.55	18.08	1 :1,000
p- ,,	213°	18.55	18.60	1 :2,000
α-Naphthylamine	202°	14.24	14.40	1 :2,000
β- ,,	180°	14.24	13.90	1 :3,000
Benzidine	176°	16.40	16.08	1 :2,000
o-Aminobenzoic acid	Above 300°	13.95	13.71	1 :3.000
m- ,,	235°	13.95	13.65	1 :5,000
p- ,,	238°	13.95	13.77	1 :3,000
pp'-Diaminodiphenyl-sulphone	170	16.50	16.85	1 :2,000

A few other azo dyes were prepared by coupling the diazotised bases with the methylol derivative of P A S, which was prepared by the condensation of one molecule of P A S hydrochloride with one molecule of formaldehyde. The reaction mixture was stirred for an hour when the methylol compound was obtained. It was washed with dilute HCl, dissolved in ammonia and reprecipitated with dilute acetic acid and finally recrystallised from methyl alcohol. The compound decomposed at 210° and for a molecular formula $C_8H_9O_4N$ it should contain 7.6% of nitrogen theoretically. Actually 7.65% N was found. It can be represented by



The melting points and nitrogen estimations of the azo dyes obtained by coupling the diazotised solutions of the following bases with alkaline solution of the methylol derivatives of P A S were active only up to 1:1,000 towards *E. Coli* and *M. phlei*, the maximum effective dilution in case of *Staph. aureus* being noted against each compound.

TABLE II

Bases diazotised.	Decomp. pt.	% Nitrogen. Calc.	Found.	M.E.D. Staphlo.
Aniline	130°	14.6	15 58	1 :3,000
o-Toluidine	240°	13.9	14.68	1 :4,000
m- ,,	265°	13.9	13.19	1 :2,000
p- ,,	245°	13.9	13 25	1 :4,000
o-Chloroaniline	110°	13.03	13.35	1 :3,000
p- ,,	130°	13.03	13.61	1 :4,000
P A S				< 1 :1,000

As the activities of the simple azo dyes described above were not of a high order, it was decided to prepare their mercurated derivatives. The mercurated azo dyes were prepared by coupling a number of diazotised mercurated bases with P A S in acetic acid medium.

The mercurated bases used were prepared by taking the amines in alcohol and adding an equimolecular quantity of HgO in dilute acetic acid. A precipitate appeared in some cases immediately, and in some cases gradually on standing. The mixture was kept in the refrigerator for 24 hours. It was collected, washed with warm dilute alcohol and finally with water. Mercury was estimated by the gold crucible method.

The melting points and amounts of Hg in the following mercurated bases, which were subsequently used in preparation of the mercurated azo dyes, are tabulated below.

TABLE III

$X = HgOCOCH_3$.

Bases prepared.	M.p. (lit) * Calc.	M.p. (Found).	% Mercury Calc.	Found.
2 :4-Di-X-aniline	209°	211°	65.68	63.00
5-X-*o*-toluidine	144°	148°	63.80	64.10
6-X-*m*- ,,	176°	174°	54 00	54 80
3-X-*p*- ,,	184°	186°	54.60	54.80
4-X-*p*-Chloroaniline	—	190°	52.10	51.80
2 :4-Di-X-α-naphthylamine	—	Above 260°	59.80	60.70
X-β-Naphthylamine	—	182°	49.50	49 99

* "Whitmore, Text-book of Mercury Compounds".

The mercurated azo dyes were prepared by taking 0.02 *M* of the base, dissolved in two and half equivalents of acetic acid and the solution was diazotised by adding $NaNO_2$ solution dropwise below 5° till the mixture turned the starch-iodide paper blue. The resulting diazonium acetate solution was added to P A S (0.02*M*), dissolved in alcohol (0.02*M*) and acidified with acetic acid. A solution of 5 g. of sodium acetate in 30 c.c. of water was stirred for half an hour till the precipitate settled down. It was crystallised from 80% acetic acid, dried in a vacuum desiccator and the Hg estimated by the gold crucible method.

The melting points and estimations of Hg in the mercurated azo dyes obtained by coupling the diazotised mercurated bases with P A S in acetic acid medium are given in Table IV. Their activities towards various organisms are noted against each.

TABLE IV

X = $HgOCOCH_3$.

Bases diazotised.	Decomp. pt.	% of Mercury.		M. R. D.		
		Calc.	Found.	*E. Coli.*	*M. phlei.*	*Staph.*
2:4-Di-X-aniline	210°	51.80	52.70	1 : 28,000	1 : 28,000	1:480,000
5-X-*o*-toluidine	195°	39.80	40.50	1 : 28,000	1 : 30,000	1:500,000
6-X-*m*- ,,	185°	39.80	40.18	1 : 98,000	1:480,000	1:480,000
3-X-*p*- ,,	178°	39.80	40.70	1:120 000	1:500,000	1:500,000
4-X-*m*-Chloroaniline	200°	36.50	36 90	1 : 98,000	1:450,000	1:480,000
2-X-*p*- ,,	190°	36.50	37.20	1:120,000	1:420,000	1:520,000
2:4-di-X-α-naphthylamine	188°	48.60	49.30	1 : 30,000	1:530 000	1:610,000
X-β-naphthylamine	198°	35.80	36.50	1 : 20,000	1:430,000	1:580,000
Mercurated P A S	205°	56.08	56.82	—	—	1 : 80,000

Thus it is seen that the mercurated azo dyes of P A S are very active towards the organisms tested above, specially towards *Staph. aureus*.

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METALLIC SALTS OF MERCURI-ARYLOXYACETIC ACIDS AND THEIR MAGNETIC PROPERTIES

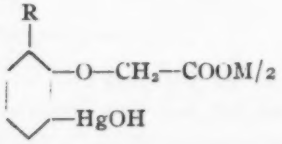
By Sachindra Kumar Dutta and Gurupada Banerjee

A number of bimetallic salts of aryloxyacetic acids, e g., phenoxy-, *o*-cresoxy- and guaiacoxy-acetic acids, with mercury and copper, nickel and cobalt, have been prepared and their properties studied. Their structures have been elucidated from a study of their magnetic properties.

It is known that aryloxy-fatty acids can be mercurated by various methods (cf. Guha Sircar and Dutta, this *Journal*, 1950, **27**, 357) with common mercurating agents like HgO, HgOAc, etc. and mercury enters the ring forming a true organometallic compound. The structure (I) has been given to the mercury compound of phenoxy-acetic acid (Whitmore, "Organic Compounds of Mercury", 1921):

(I) (II)

With alkali it gives a sodium salt, represented by structure (II) . In our preliminary investigation, it was found that on adding a concentrated solution of copper sulphate to the aqueous solution of the sodium salt of hydroxymercuri-phenoxyacetic acid, a geenish blue precipitate was formed. Though it was expected to be an inner-bimetallic complex at the beginning, from the study of its properties, e. g., colour, solubility and magnetic properties, it proved to be a simple salt, later. Sodium salts of hydroxymercuri-cresoxy- and -guaiacoxy-acetic acids etc., were also found to give similar compounds with copper. Again, with bivalent Ni and Co, the above mercury compounds gave rise to similar type of bimetallic salts. These salts may be represented by the following general formula:



(where R = H, CH_3 or OCH_3 and M = Cu, Ni, Co)

The compounds are insoluble in water and in all organic solvents. They are also insoluble in all mineral acids. On treatment with boiling dilute hydrochloric acid, the compounds decomposed into the metallic chlorides, $HgCl_2$ and the corresponding aryloxy-acetic acids, showing their unstability. The organic residue was eliminated by heating the compounds under reflux with H_2O_2 in presence of H_2SO_4 for about 20 minutes until the solution was clear, the excess of H_2O_2 being removed by $KMnO_4$ solution.

Mercury and the other metals were then estimated as usual. The analytical data obtained supported the structures assigned. Like all other mercuric salts, the aryloxy-mercuri compounds have been found to be diamagnetic. Measurement of magnetic susceptibilities of the bimetallic compounds, described in this paper, was also made with a view to elucidating their structures. The results are shown in Table 1.

EXPERIMENTAL

The aryloxyacetic acids were prepapred from the appropriate phenol and chloro-acetic acid (*J. Amer. Chem. Soc.*, 1931, **53**,304; 1943, **65**, 1555). They were crystallised from hot water until no further change could be seen in their melting points. The aryloxyacetic acids were mercurated with mercury acetate, as described by Guha Sircar and Dutta (*loc. cit.*).

Copper Salt of Hydroxymercuri-phenoxyacetic Acid.—The hydroxymercuri-phenoxyacetic acid was dissolved in dilute acetic acid and was neutralised with a solution of NaOH. On adding a concentrated solution of copper sulphate a voluminous greenish blue precipitate was formed at once. This was filtered, washed thoroughly with cold water and dried at 105°. The compound is insoluble in water and in all organic reagents; it decomposes on heating with acids and alkalies. (Found: Cu, 7.90; Hg, 50.02. Calc. Cu, 7.95; Hg, 50.23 per cent).

Nickel salt of hydroxymercuri-phenoxyacetic acid was prepared like the above compound using nickel sulphate in place of copper. It resembles the copper compound in properties. (Found: Ni, 7.35; Hg, 50.86. Calc. Ni, 7.39; Hg 50.47 per cent).

Cobalt salt of hydroxymercuri-phenoxyacetic acid was prepared by heating a solution of cobalt chloride with the neutral solution of the mercury compound. The light blue cobalt compound resembles the corresponding compounds of copper and nickel in properites. (Found: Co, 7.61; Hg, 50.89. Calc. Co, 7.42; Hg, 50.52 per cent).

Copper Salt of Hydroxymercuri-o-cresoxyacetic Acid.—To a neutral solution of the *o*-cresoxy-mercuri compound, a concentrated solution of copper sulphate was added when a pale blue precipitate was formed. The compound was washed and dried as before. (Found: Cu, 7.38; Hg, 48.13. Calc. Cu, 7.66; Hg, 48.54 per cent).

Nickel salt of hydroxymercuri-o-cresoxyacetic acid was obtained as a light green precipitate from a mixture of nickel sulphate solution and a neutral solution of the mercury compound, on heating on a water-bath. (Found: Ni, 7.18; Hg, 48.12. Calc. Ni, 7.13; Hg, 48.75 per cent).

Cobalt salt of hydroxymercuri-o-cresoxyacetic acid was prepared from cobalt chloride and the mercuri compound like the corresponding copper salt. It is light pink in colour and resembles the previous compounds. (Found: Co, 7.23; Hg. 48.73. Calc.Co, 7.17; Hg, 48.80 per cent).

Copper salt hydroxymercuri-guaiacoxyacetic acid was formed as a bluish white precipitate, like the previous copper compounds, from a solution of copper sulphate and the mercuri compound. It decomposes into CuO and HgO on treatment with boiling alkali. (Found: Cu 7.63; Hg 46.03. Calc. 7.42; Hg, 46.90 per cent).

Nickel salt of hydroxymercuri-guaiacoxyacetic acid was prepared by using a solution of nickel sulphate as in the case of the previous compound. It separated as a light green precipitate. (Found: Ni, 6.59; Hg, 46.38. Calc. Ni, 6.86; Hg, 46.93 per cent).

Cobalt salt of hydroxymercuri-guaiacoxyacetic acid was obtained as in the previous cases by using a solution of cobalt salts. It forms a light blue powder on drying and is unstable towards acids and alkalies, as usual. (Found: Co, 6.86; Hg, 48.63. Calc. Co, 6.90; Hg, 48.14 per cent).

Measurement of Magnetic Susceptibilities.—The susceptibilities of the aryloxy-mercuri compounds and their bimetallic salts were measured according to Gouy's method with a field strength of 9.5×10^3 gauss. The molecular susceptibility was corrected for atomic and ionic diamagnetism. From the corrected atomic susceptibility for the central metal ion, the value of its magnetic moment was calculated from the relation

$$\mu_B = 2.84 \times \sqrt{\chi_A \times T}$$

in terms of Bohr magnetons. Results are tabulated below.

TABLE I

Temp. = 24°.

	Substance.	Colour	$\chi_g \times 10^{-6}$.	$\chi_M \times 10^{-6}$.	$\chi_A \times 10^{-6}$.	μ_B.
1.	Phenoxy-mercuri compound		-0 9341	-295 41		Dia
2.	*o*-Cresoxy-mercuri ,,		-0.9032	-284.31		,,
3.	Guaiacoxy-mercuri ,,		-0.8992	-295.6		,,
4.	Cu-phenoxy-mercuri ,,	Greenish blue	2.605	2078	2243.7	2.31
5.	Cu-*o*-cresoxy-mercuri ,,	Light blue	2.467	1851	2041.0	2.29
6.	Cu-guaiacoxy-mercuri ,,	Bluish white	1.928	1657	1851.6	2.09
7.	Ni-phenoxy-mercuri ,,	Green	5.453	3994	4160.2	3.13
8	Ni-*o*-cresoxy-mercuri ,,	Light green	5.541	4547	4737.0	3.36
9.	Ni-guaiacoxy-mercuri ,,	Do	5.690	4864	5058.6	3.45
10.	Co-phenoxy-mercuri ,,	Light blue	18.89	14980	15140 7	5.98
11.	Co-*o*-cresoxy-mercuri ,,	Light pink	17.02	14010	14200.0	5 79
12.	Co-guaiacoxy-mercuri ,,	Violet	15.85	13550	13744.6	5.69

It may be noticed from the above table that the moment values of the copper compounds lie between 2.09 and 2.31, which agrees more or less with that of Cu^{++} ion in simple cupric salts, viz., 1.90 to 2.20. The nickel compounds show moments between 3.13 and 3.45 indicating the presence of two unpaired electrons as in simple nickel ion, whose moment varies from 3.20 to 3.44. The same holds good with cobalt compounds, whose moment varies between 5.69 and 5.98 which are considerably higher than that for Co^{++} ion in simple cobaltous salts, the moment of which lies between 4.5 and 5.0. The observed higher magnetic moments of the cobaltous salts are probably due to unquenching effect of the orbital magnetic moment. For, in these compounds electrons are not promoted to the higher levels and they are not effectively exposed to the fields of neighbouring atoms and ions.

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A CRITICAL STUDY OF THE VARIOUS METHODS OF EVALUATING PARACHOR. PART I

By W. V. Bhagwat and S. N. Kaveeshwar

Gibling's method of group parachor is criticised on the ground that it aims at equating the experimental values with the calculated ones rather than being useful for elucidating doubtful structures. The CH_2- differences in homologous series do not increase as the series is ascended, as assumed by Gibling, and hence, the 'Expansion correction' is purely arbitrary. Further, the values attributed to *ortho*, *meta* and *para* positions have no justification as they are not found to be constant and that they are of the same order as the error possible in determining parachor.

Attemptimg to correct the values first given by Sugden (*J. Chem. Soc.*, 1924, 1185) special mention may be made of the work of Mumford and Phillips (*ibid.*, 1929, 2122), Desreux (*Bull. Soc. chim. Belg.*, 1935, **44**, 249), Bayliss (*J. Amer. Chem. Soc.*, 1937, **59**, 444), Quayle and co-workers (*ibid.*, 1938, **60**, 2716), Gibling (*J. Chem. Soc.*, 1941, 299), Vogel (*ibid.*, 1934, 333) and by Bhagwat and co-workers (this *Journal*, 1945, **22**, 116, 221). Mumford and Phillips (*J. Chem. Soc.*, 1950, 75) and Telang (*J. Amer. Chem. Soc.*, 1949, **71**, 1884, 1898) have again opened the subject of atomic and structural parachors. Since a vast amount of parachor data at various temperatures is now available as compared to what existed when Sugden (*loc. cit.*) initiated the subject of parachor, we have thought it advisable to study critically the various existing views.

Gibling (*loc. cit.*) has discarded the conception of atomic parachor and has introduced the idea of group parachors. Thus he attributed values to every possible group. Again, he has two sets of values, corrected and uncorrected. Further he has values for α, β, γ, δ, and *o*, *m*, *p* positions of the same group. The most empirical thing in his method is the addition of a certain value, known as the expansion correction, to the standard value obtained in each case from the structural values of the group parachors.

The fundamental aim in deriving atomic and structural parachors is to use them for establishing doubtful molecular structures. When values are attributed to every possible group and to its every possible position, it only aims at reproducing the experimental results, and thus its application in doubtful cases is extremely limited. Further, it is doubtful in certain cases whether the structural values given can have any specific importance. The case of *ortho*, *meta* and *para* compounds may be taken as an example. We have collected the data from the other workers and some of them are shown below.

TABLE I

Compound.	Observed parachor. *ortho.*	*meta.*	*para.*	Parachor differences *o*—*m*.	*m*—*p*.	*p*—*o*.
Chlorotoluene	280.8	...	283.6	...	...	+2.8
Nitrotoluene	301.1	300.6	301.6	+0.5	−1.0	+0.5
Nitroanisole	320.5	...	322.0	...	...	+1.5
Chloronitrobenzene	299.9	298.9	300.0	+1.0	−1.1	+0.1
Bromonitrobenzene	312.9	313.5	313.5	−0.6	±0.0	+0.6
Xylene	283.3	284.6	283.8	−1.3	+0.8	+0.5
Methoxyazobenzene	486.9	486.9	485.0	±0.0	+1.9	−1.9
Nitrophenol	273.2	283.3	280.8	−10.1	+2.5	+7.6
Hydroxybenzaldehyde	268.0	274.5	278.2	−6.5	−3.7	+10.2
Tolnylazoimide	303.8	...	307.0	...	...	+3.2
Cresol	257.5	257.1	...	+0.4	...	...
Toluidine	269.3	...	272.4	...	...	+3.1
Tolunonitrile	292.5	295.6	295.2	−3.1	+0.4	+2.7
Xylene	282.41	284.21	284.45	−1.80	−0.24	+2.04
Ethylmethylbenzene	319.88	322.83	323.30	−2.95	−0.47	+3.42
Diethylbenzene	357.64	361.01	361.39	−3.37	−0.38	+3.75
Gibling's values	−2.7	−1.7	−2.2	−1.0	+0.5	+0.5

These results clearly show that it is impossible to attribute any definite value for the *o*, *m* and *p* positions, since the differences *o-m*, *m-p*, and *p-o* are not only not constant and vary widely, but sometimes they vary in sign as well. Gibling's values −2.7, −1.7 and −2.2 for *o*-, *m*- and *p*- positions therefore serve no purpose. These values suggest that *meta*-compounds should have the highest parachor. The above table will show that in a number of cases the values for *para*-compounds are higher. This is true of the *ortho*-compounds also in some cases.

According to Sugden 0.5% error in the measurement of parachor is possible, while other workers admit an error of 0.2%. As all the above values are near about 300, an error of 0.6 to 1.5 units is not unexpected. The differences in parachor of *o*-, *m*- and *p*- compounds in many cases are of this order and the differences between the values for these compounds given by Gibling are also of the same order. No values therefore can justifiably be attributed to them.

The 'Expansion correction' of Gibling is purely empirical and is based on the assumption that the value of CH_2 in homologous series goes on increasing as we ascend the series. This is far from the truth.

TABLE II

Hydrocarbons.	Para-chor.	Diff. CH_2.	Ethyl esters. Compounds.	Para-chor.	Diff. CH_2	Methyl esters. Para-chor.	Diff. CH_2.	Malonic esters. Compound.	Para-chor.	Diff. CH_2
Ethane	110.5		Malonate	361.5		283.0		Dimethyl	355.8	
		39.4			38.5		38.3			35.5
Propane	149.9		Succinate	400.0		321 3		Methylethyl	391.3	
		40.4			3).6		40.1			39 9
n-Butane	190.3		Glutarate	439 6		361 4		Methyl-*n*-propyl	431.2	
		2 × 40.05			40.6		40.4			37.6
n-Hexane	270.4		Adipate	480.2		401.8		Ethyl-*n*-propyl	468.8	
		39.6			40.3		41.5			36.3
n-Heptane	310.0		Pimelate	520.5		443.3		Di-*n*-propyl	505.1	
		40.6			42.3		41.1			
n-Octane	350.6		Suberate	562.8		484 4				
					2 × 40.5		40.2			
			Sebacate	643.8		524.6*				

Fluorides.			Dichlorides.			Dibromides.	
n-Amyl	241.6		Methylene	147.5		175.1	
		40.4			41.3		40.3
n-Hexyl	282.0		Ethylene	188.8		215.4	
		2 × 39.6			37.8		37 9
n-Octyl	361.3		Propylene	226.6		253 3	

* Figure refers to methyl azelate.

Similar observations have been made in case of alkyl chlorides, bromides and iodides, in normal alkylbenzenes, ketones, etc. (cf. Vogel, *loc. cit.*).

It will be clear therefore that there is no basis for 'Expansion correction', which increases as the molecular weight increases, and becomes enormous for very large molecules.

The correction for α-, β-, γ- and δ- position of groups are identical with *o*-, *m*- and *p*- position of groups and can be dealt with similarly. We therefore conclude that Gibling's group parachors aim more at equating the observed values with calculated ones and is no advance in the direction of their use for elucidating molecular structures in doubtful cases. Other points of criticism which are common with other methods will be considered jointly with them.

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HYDROGEN BONDING BETWEEN ETHERS AND ALCOHOLS WITH THE HELP OF PARACHOR

By W. V. Bhagwat, S. N. Kaveeshwar and P. H. Trivedi

The parachors of diethyl, phenylmethyl and *p*-cresylmethyl ethers in alcohols show an appreciable decrease which confirms the existence of the compounds of the type R_2O :: H.O.R′ by hydrogen bond.

Moore and Winmill (*J. Chem. Soc.*, 1912, **101**, 1635), Latimer and Rodebush (*J. Amer. Chem. Soc.*, 1920, **42**, 1419), Lowery (*J. Chem. Soc.*, 1923, **123**, 822) and Sidgwick (*ibid.*, 1924, 527, 2672) suggested that hydrogen atom under certain conditions could increase its co-valency by one. Pauling (*J. Amer. Chem. Soc.*, 1935, **57**, 2680) however, has shown on the basis of quantum mechanical theory of valency that hydrogen atom with only one stable orbital, cannot form more than one pure co-valent bond and that the hydrogen bond is electrostatic in character. It was observed by Sidgwick (*J. Chem Soc.*, 1930, 1461, 2027) in case of *o*-nitrophenols that there was a decrease in parachor. He wrongly attributed it to an increase in co-valency of hydrogen. We suggest that the decrease is due to hydrogen bonding and since the strength of the hydrogen bond depends upon the groups attached to it, this value should vary. Bennet and Phillips (*ibid.*, 1928, 1830, 1937) have studied the solubility of ethers in water and have confirmed the view that the presence of electron-repelling groups tends to increase the solubility; the evidence is thus in favour of hydrogen bonding. It is suggested (cf. Glasstone, "Recent Advances in Physical Chemistry, 1938, p. 49) that an oxygen atom in an ether can combine with hydroxylic derivatives to form compounds of the type R_2O . . . . H.O.R′. We have tried to investigate this point from the study of parachor. If such a union occurs, an appreciable decrease in parachor is expected. Methyl alcohol, ethyl alcohol, *iso*propyl alcohol, amyl alcohol and phenylmethyl ether, diethyl ether and *p*-cresylmethyl ether were used.

Experimental

Surface tension of liquids was determined by the maximum bubble pressure method, as recommended by Sugden (*J. Chem. Soc.*, 1924, 1185) ; the density was found by a pyknometer and the constancy of temperature maintained was ± 0.1°. The liquids were twice distilled and their purity confirmed by their boiling points.

The procedure adopted consisted in finding out the parachors of ethers and alcohols separately and then of ethers in alcohols. The values obtained in solution were then compared with those observed for pure liquids. This method balances any error due to personal factor, and due to presence of slight impurity. The method may involve a slight deviation from absolute values, but the net conclusion remains unaffected.

TABLE I

Parachors of ethers and alcohols.

Methyl alcohol	82.2	Phenylmethyl ether	234.7
Ethyl alcohol	125.9	*p*-Cresylmethyl ether	299.0
*iso*Propyl alcohol	162.0	Diethyl ether	210.5
Amyl alcohol	234.7		

The parachor of solute in solution was determined by the Hammick and Andrew equation (*J. Chem. Soc.*, 1929, 754; 1930, 1876; 1934, 32; 1935, 207):

$$P_m = xP_x^{\frac{1}{4}} + (1-x)\,P_s$$

where P_m is the parachor of the solution $= \dfrac{M_m r^{\frac{1}{4}}}{D}$ and M_m is given by

$$M_m = xM_x + (1-x)\,M_s$$

where x is the molecular fraction of the solute, $1-x$, the molecular fraction of the solvent, P_x and P_s, the parachors of the solute and the solvent respectively, r, the surface tension of the solution whose density is D; M_m is the mean molecular weight and M_x and M_s are the molecular weights of the solvent and the solute respectively.

TABLE II

Parachor of phenylmethyl ether in alcohols.

Solvent.	x.	M_m.	t.	D.	r.	P_m.	P_x.
MeOH	0.1855	46.13	40°	0.8612	23.84	118.4	255 8
	0 4804	68.58	20°	0.9393	28.80	168.0	255.4
	0.5471	73.78	20°	0.9505	29.88	179.5	255 9
	0.6203	79.23	20°	0.9832	29.35	191.8	254.6
EtOH	0 1622	56.14	20°	0.8555	24.52	146.1	252.9
	0.2408	61.01	20°	0.8748	25.32	156.4	253.5
	0.3468	67.59	20°	0.8999	26.37	170.2	254.2
*iso*Pr OH	0.2015	69.77	19°	0.8439	22.76	180.5	253 6
	0.2911	74.07	20°	0.8660	23.90	189.1	254 9
	0.5102	84.60	20°	0.9109	25.30	208.3	252.9
	0.5657	87.26	21°	0 9189	26.42	215.3	255 7
	0.6720	92.20	20°	0.9430	27.31	223.9	253.9
Am.OH	0 3233	94.61	20°	0.8732	25.22	242.9	256.6
	0 5512	99.17	22°	0.9111	26.17	246.4	254.7
	0.6526	101 19	20°	0.9285	26.83	248.0	254.2

TABLE III

Parachor of p-cresylmethyl ether in alcohols.

Solvent.	x.	M_m.	t.	D.	r.	P_m.	P_x.
MeOH	0 3334	62.07	40°	0 8835	23.61	154.9	287.8
	0 4079	68.79	21°	0.9160	26.40	170.2	289.7
EtOH	0.1900	60.54	21°	0.8565	24.02	156.5	288.4
	0.2138	62.33	30°	0.8572	23.67	160.3	287.0
	0.2671	66.39	20°	0.8616	23.47	169.6	290 3
	0.3755	74.63	19°	0.8997	25.77	186.9	288.8
	0.4294	78.73	22°	0.9252	25.69	196.0	288.9

TABLE IV

Parachor of diethyl ether in alcohols.

	x.	M_m.	t.	D.	r.	P_m.	P_x.
MeOH	0.3927	48.56	21°	0.7548	18.06	132 9	202.5
EtOH	0.3175	54.97	22°	0.7661	18.82	149.4	200.5
	0.3543	56.01	22°	0.7625	18.56	152.5	201.3
iso-Pr.OH	0.6298	68.92	23°	0.7362	17.19	187.8	202.5

Our parachor results indicate that when phenylmethyl ether is dissolved in alcohols its parachor value is about 254, while the observed value of the pure liquid is 263. Similarly the values for the *p*-cresylmethyl ether and the diethyl ether in alcohols are approximately 288 and 202 respectively, while the corresponding values for pure liquids are 299 and 211. It is clear therefore that there is an appreciable fall in parachor by about ten units, when the ethers are dissolved in alcohols. The experiments therefore confirm the view of Glasstone (*loc. cit.*) and of Bennet and Phillips (*loc. cit.*) that the compounds of the type $R_2O....H.O.R'$ by hydrogen bonding are formed.

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STUDIES ON *p*-AMINOSALICYLIC ACID DERIVATIVES. PART II. ALDEHYDE-BISULPHITE COMPOUNDS

By Satchidananda Patnaik and S. S. Guha Sircar

A few aldehyde-bisulphite condensation products of P A S, on the lines of diasone, promine and sulphetrone from DADPS, have been prepared and also mercurated and all the products tested against common bacteria like *Staphylococcus aureus*, *E. Coli* and *Mycobcaterium phlei* in Kirchner's synthetic medium. The unmercurated compounds, were found to have low activities against these bacteria. The mercurated compounds, however, were active in dilutions varying from 1 :30,000 to 1 :120,000. A few of the active products were tested for biochemical antagonism in the presence of PABA, nicotinic acid and cysteine.

In the present work an attempt has been made to prepare aldehyde-bisulphite compounds of P A S, on the lines of diasone, promine and sulphetrone from DADPS, in order to unite high activity with low toxicity. Only the formaldehyde-bisulphite compound has been described in the literature (Hirt and Hurni, *Helv. Chim. Acta*, 1949, **32**, 378)

The aldehyde-bisulphite compounds of P A S were tested against common bacteria like *E. Coli*, *Staphylococcus aureus*, *Mycobact. phlei*, the first one being gram-negetive and the last two being gram-positive; the last one being also acid-fast is comparable to *Mycobact. tuberculosis*. The aldehyde-bisulphite compounds of P A S were found not to be very active against these bacteria (activity found only in 1:1,000 dilution).

All the products have been mercurated with the help of mercuric acetate using the standard method of mercuration. The derivatives have been found to be quite active against the above mentioned organisms. Hence, the introduction of mercury helps in augmenting the antibacterial action.

A few of the more active mercurated compounds have been tested for biochemical antagonism when used against *E. Coli* and *Staphylococcus aureus* in the presence of the metabolites PABA, nicotinic acid and cystiene.

The first two metabolites have been found to antagonise the effect of some other groups of antibacterial compounds, especially the sulpha drugs. The idea of using cysteine was to see whether the presence of sulphur in this form could make the mercury in the drug inactive. The definite antagonism caused by these metabolites was proved in each case by the fact that the concentration of the antibacterial mercurial that prevented the growth of the microbe in the absence of any of them, was not sufficient to do so, when any one them was present in 1:5 (wt./wt.) ratio, in the solution of the mercurial in contact with the microbe, a much higher concentration being necessary to suppress the bacterial growth (vide Table IV).

The antibacterial tests were carried out by the Rideal-Walker serial dilution method in Kirchner's synthetic medium since ordinary broth medium, prepared from 'lemco' contained detectable amounts of PABA, which was known to act as an antagonist to PAS

and some of its derivatives, thus decreasing the real activity of the drug and increasing the rate of growth of the baceria to which PABA was known to act as a metabolite.

In the presence of groups like NO_2, OH, the activity was considerably reduced as compared to groups like NH_2. Similar observations have been made by Eagle, Hogan and Doak about the influence of acidic groups on the trypanocidal action of phenyl arsenoxides ("Advancing Fronts in Chemistry, Vol. II, Chemotherapy", p.131). The order of activity due to different substituents can be stated as

$$-Cl, \quad -N(CH_3)_2, \quad -NH_2, \quad -OCH_3 \quad -OH, \quad -NO_2.$$

Similar observations have also been made by Guha Sircar and co-workers (this *Journal*, 1950, **27**, 537; 1953, **30**, 359 et seq.).

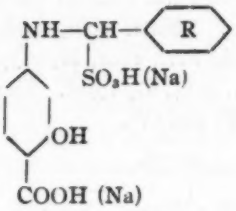
Experimental

The free acid P A S and its hydrochloride are unstable and undergo decarboxylation on prolonged heating even at 60°-70° or in solutions (especially in light) to give *m*-aminophenol. On the other hand, the monosodium salt of P A S was found to be less sensitive to heat and the Hugo Bauer method No 2. of preparation of diasone from DADPS (*J. Amer. Chem. Soc.*, 1939, **62**, 617) was used with a slight modification.

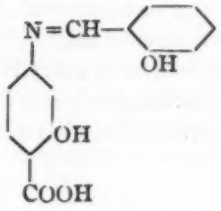
Equimolecular quantities of Na-PAS and the aldehyde-bisulphite compound were warmed for about 2 hours on a water-bath at 50° to 60° with the minimum amount of water. The contents were then cooled in ice and the free acid was precipitated by adding dilute hydochloric acid in slight excess.

Some loss of sodium bisulphite took place when the aldehyde-bisulphite compound was used after its isolation; so the reaction had to be carried out in presence of a slight excess of the reagent. On the other hand, the derivative did not precipitate out immediately after addition of the acid when a large excess of sodium bisulphite was used and the compound appeared only on long standing in the refrigerator.

In actual practice, to 10 c.c. of an aqueous solution containing about 1.5 g. (1/80 th) of sodium bisulphite was added 0.01*M* of the aldehyde and the mixture shaken well for ½ hour to ensure complete formation of the additive compound. To this was added 2.2 g. (0.01*M*) of Na-PAS and the mixture warmed for about 2 hours at 50°-60°. The contents were then cooled in ice and the free acid was precipitated by the slow addition of dilute HCl. In most cases a gummy product was obtained which was treated with ether to make it granular. The first purification was made by dissolving the compound in dilute ammonia and reprecipitating it by adding dilute HCl and finally recrystallising the separated solid from dilute alcohol. In case of *m*-nitrobenzaldehyde, cinnamic aldehyde, *o*-chlorobenzaldehyde, the free acid was more soluble and so the Na salt was isolated first by adding 30 c.c of absolute alcohol to the reaction mixture after cooling. The purification was done by dissolving the Na salt in minimum amount of water and reprecipitating it by adding alcohol. The free acid and the sodium salt can be represented by formula(I).



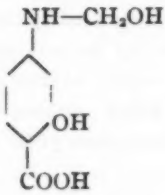
(I)



(II)

[where R is OH, NO_2, $N(CH_3)_2$, Cl and $-OCH_3$ group in *ortho*, *meta* or *para* positions of the aldehyde nucleus]. In case of salicyaldehyde, however, the anil was obtained, as there was desulphonation on acidification. The salicylaldehyde compound can be represented by formula (II) and is therefore not comparable to other members of the series.

Condensation with formaladehyde was done in a different manner in order to get the methylol compound rather than the anil. The hydrochloride of P A S (1.9 g.) was stirred well with 4 c.c. of formalin containing equimolecular proportion of formaldehyde for one hour, when the methylol compound was obtained. The product was dissolved in ammonia, reprecipitated with dilute acetic acid and finally recrystallised from methyl alcohol. It can be represented by formula (III).

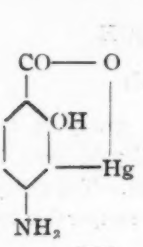


(III)

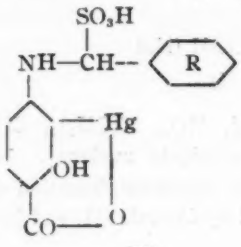
Table I gives the list of the aldehydes condensed, the melting points of the products and their analytical data.

The compounds (0.02*M* of each) were mercurated by the addition of mercuric acetate solution (1.5 g of mercuric acetate dissolved in 5 c.c. of water containing a few drops of dilute acetic acid) to an alcoholic solution of the compound at the ordinary temperature. The precipitate separated out almost immediately and the contents kept after a little shaking in the refregerator overnight to ensure complete reaction. The precipitate was filtered, and washed with a little hot dilute alcohol and with water. The first purification was made by dissolving the residue in dilute alkali and reprecipitating with dilute acetic acid and crystallising the precipitate from glacial acetic acid. In cases where the sodium salt of PAS-aldehyde bisulphite condensation product was used, it was dissolved in water, acidified with acetic acid, and mercuric acetate solution was then added. Besides PAS derivatives, PAS itself was also mercurated by this method.

In most cases the mono-mercuri derivative (which was desired) was obtained and mercury entered in the form of anhydro mercuri group. Similar compounds have been obtained by the mercuration of salicylic acid (Dimroth, *Ber.*, 1902, **35**, 2837),anthranilic acid, PABA and *m*-aminobenzoic acid (Scoeller, *Ber.*, 1914, **47**, 1930). Hence mercurated PAS and PAS derivatives can be represented as (IV) and (V).



(IV)



(V)

On shaking these compounds with potassium iodide solution and filtering, no red colour was obtained on adding ferric chloride solution to the filtrate, showing the absence of acetoxymercuri group in the compound. Bromine water, however, split off Hg from the nucleus. No HgS was formed on passing H_2S into the solution at room temperature. Hydrazine sulphate had also no reducing action in the cold.

Table II gives a list of compounds mercurated, their melting points and analytical data. Nitrogen in the compounds was estimated by the gold crucible method.

The results of biological tests indicating the maximum effective dilution (M.E.D) of the active compounds at 10 minutes' contact against different organisims are shown in Table III. The organisms were a 48 hours' culture of *E.Coli* and *Staph.aureus* in nutrient peptone broth at 37° and *Mycobacterium phlei* in Kirchner's synthetic medium, also at 37°.

Sri J. L. Ghose, Research Assistant under a B.S.I.R., Orissa, scheme of research, has actively taken part in the biological studies.

TABLE I

Name of the aldehyde.	Symbol.	M. p.	Mol. formula.	%Nitrogen. Found.	Calc.
Benzaldehyde	1	190° (d)	$C_{14}H_{11}O_6NS$	3 7	4·3
Salicylaldehyde	2	175°	$C_{14}H_{11}O_4N$	5·2	5·45
Anisaldehyde	3	199° (d)	$C_{15}H_{15}O_7NS$	3·62	3·96
p-Nitrobenzaldehyde	4	180° (d)	$C_{14}H_{12}O_8N_2S$	7·26	7·6
m-Nitrobenzaldehyde	5	231° (d)	$C_{11}H_{10}O_8N_2SNa_2$	6·3	6·45
p-Dimethylaminobenzaldehyde	6	177° (d)	$C_{16}H_{18}O_6N_2S$	7·5	7·64
Vanillin	7	136° (d)	$C_{15}H_{15}O_8NS$	3·2	3·7
Formaldehyde	8	210° (d)	$C_8H_9O_4N$	7.65	7.6
p-Hydroxybenzaldehyde	9	217° (d)	$C_{14}H_{13}O_7NS$	3·9	4·13
Cinnamylaldehyde	10	239° (d)	$C_{16}H_{14}O_9NS_2Na_3$	2.2	2.82
o-Chlorobenzaldehyde	11	223° (d)	$C_{14}H_{10}O_6NSClNa_2$	3·1	3·5
Furfural	12	237° (d)	$C_{12}H_9O_7NSNa_2$	3.6	3·93

The synthetic medium was prepared by dissolving 3.0 g. of disodium hydrogen phosphate, 4.0 g. of potassium dihydrogen phosphate, 0.6 g. of magnesium sulphate, 2.5 g. of sodium citrate, 5.0 g. of asparagine and 20 c.c. of glycerol, dissolved in one litre of water (redistilled water) to which was added 2 c.c. of 40% NaOH solution to make the p_H 7.2. Five c.c. of this were put into dried, plugged test tubes and these were sterilised in an autoclave for 20 minutes at 15 lbs. pressure.

TABLE II

Symbols of compounds mercurated.	Symbol of product.	M.p.	Mol. formula.	% Mercury. Found.	Calc.
PAS	HgPAS	205° (d)	$C_7H_5O_3NHg$	56.82	57.06
1	Hg.1	201° (d)	$C_{14}H_{11}O_6N8Hg$	38.1	38.46
2	Hg.2	192° (d)	$C_{14}H_9O_4NHg$	43.2	44.02
3	Hg.3	200° (d)	$C_{15}H_{13}O_7NSHg$	35.8	36.3
4	Hg.4	186° (d)	$C_{14}H_{10}O_8N_2SHg$	34.6	35.4
5	Hg.5	242° (d)	$C_{14}H_{10}O_8N_2SHg$	34.8	35.4
6	Hg.6	208° (d)	$C_{16}H_{16}O_6N_2SHg$	34.2	35.4
7	Hg.7	192° (d)	$C_{15}H_{11}O_6NSHg$	34.8	35.34
8	Hg.8	236° (d)	$C_8H_7O_4NHg$	51.9	52.55
9	Hg.9	243° (d)	$C_{14}H_{11}O_7NSHg$	37.1	37.3
10	Hg.10	260° (d)	$C_{16}H_{18}O_9NS_2Hg$	31.3	31.9
11	Hg.11	Above 280° (d)	$C_{14}H_{10}O_6NClHg$	35.3	36.1
12	Hg 12	252° (d)	$C_{12}H_9O_7NSHg$	38.5	39.2

TABLE III

Maximum effective dilution (M.E.D.).

Compound.	Staph.	Myco. phlei.	E. Coli.	Compound.	Staph.	Myco. phlei.	E. Coli.
11	1 :2,000	1 :2,000	Not tested	Hg.6	1 :100,000	1 :80,000	1 :60,000
Hg-PAS	1 :80,000	1 :80,000	1 :40,000	Hg.7	1 :50,000	1 :60,000	1 :30,000
Hg.1	1 :40,000	1 :30,000	1 :30,000	Hg.8	1 :80,000	1 :80,000	1 :60,000
Hg.2	1 :50,000	1 :50,000	1 :40,000	Hg.9	1 :40,000	1 :50,000	1 :30,000
Hg.3	1 :50,000	1 :50,000	1 :30,000	Hg.10	1 :60,000	1 :60,000	1 :40,000
Hg.4	1 :30,000	1 :40,000	1 :30,000	Hg 11	1 :120,000	1 :100,000	1 :80,000
Hg.5	1 :40,000	1 :40,000	1 :30,000	Hg.12	1 :50,000	1 :50,000	1 :30,000
				P.A.S. (Na-salt)	1 :1,000	1 :1000	

TABLE IV

Compound.	*Staphylococcus aureus*				*E. Coli*			
	I.	II.	III.	IV.	I.	II.	III.	IV
Hg-PAS	1 :80,000	1 :40,000	1 :40,000	1 :40,000	1 :40,000	1 :10,000	1 :10,000	1 :30,000
Hg. 1	1 :40,000	1 :20,000	1 :20 000	1 :30,000	1 :30,000	—	—	1 :20,000
Hg. 2	1 :50,000	1 :30,000	1 :30,000	1 :50,000	1 :40,000	1 :10,000	1 :10,000	1 :20,000
Hg. 4	1 :30,000	1 :10,000	—	1 :20,000	1 :30,000	—	—	1 :20,000
Hg. 6	1 :100,000	1 :40,000	1 :30,000	1 :50,000	1 :60,000	1 :20,000	1 :20,000	1 :50,000
Hg. 8	1 :80,000	1 :40,000	1 :30,000	1 :50,000	1 :60,000	1 :30,000	1 :30,000	1 :40,000

I—M.E.D. without antagonist. II—M.E.D. with PABA. III—M.E.D. with nicotinic acid. IV—M.E.D. with cystein.

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A NOTE ON THE RELATIONSHIP BETWEEN PARACHOR AND MOLECULAR REFRACTIVITY

By A. M. Talati

Herz (*Z. anorg. Chem.*, 1927, **159**, 316) has shown from the data available for some 51 organic liquids that the quotient of parachor divided by molecular refractivity is constant and independent of the nature of the liquid. The author has calculated the value of this quotient for numerous organic compounds and has found that

(1) a constant value 8.60 of the quotient is found in some homologous series of aliphatic compounds;

(2) in other homologous series of organic compounds in which the value of the quotient is not constant, this quotient tends to approach a value of 8.60, as the series is ascended;

(3) the presence of a phenyl group, a branched chain, or a double bond in a compound lowers the value of the quotient considerably when compared with the value of the normal compound;

(4) the value of the quotient $[P]/[R]$ of different compounds has been found to vary from 7.15 to 11.05.

This shows that when a large number of organic compounds are considered, Herz's ratio $[P] \div [R]$ does not turn out to be independent of the nature of the liquid. The author has found, however, that the ratio

$$\frac{[P]}{[R] \times (\log_{10}) [P] - \log_{10} 3[R]}$$

where $[P]$ and $[R]$ are the parachor and the molecular refractivity respectively, has a constant value 18.9 ± 0.1, independent of the nature of the liquid, with the exception of the anomalous behaviour of some methyl compounds.

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